

Supplementary material.

A Noble Nexus: A Phosphino-Phen Ligand for Tethering Precious Metals

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NMR and Mass Spectra

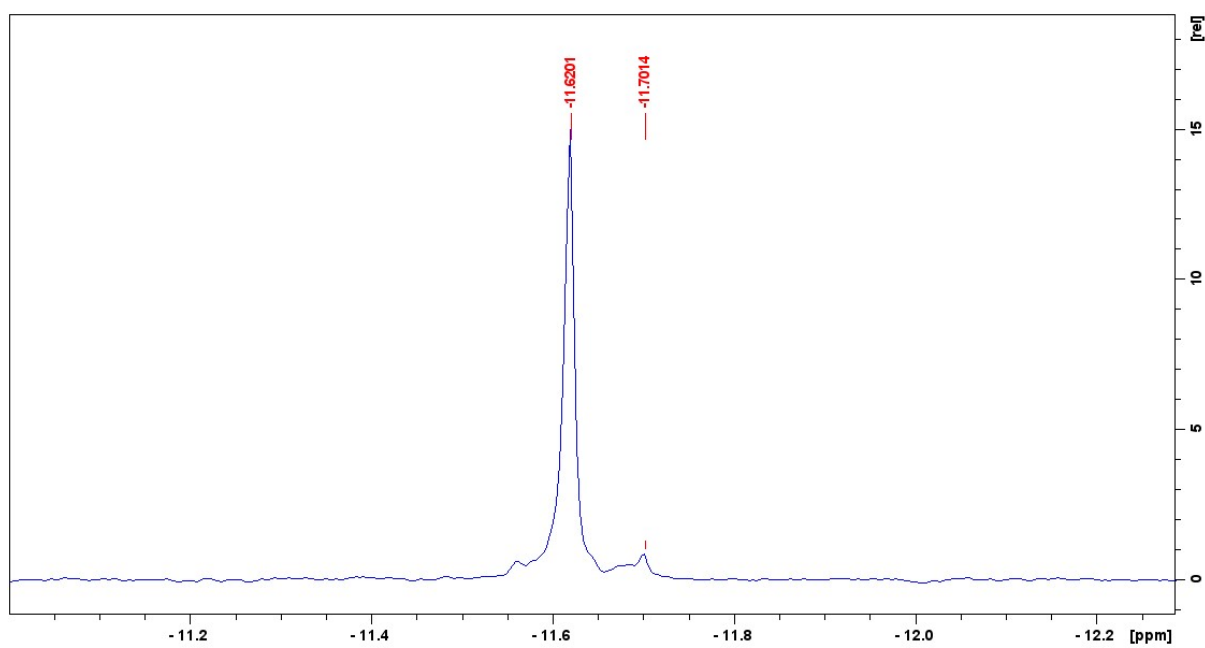
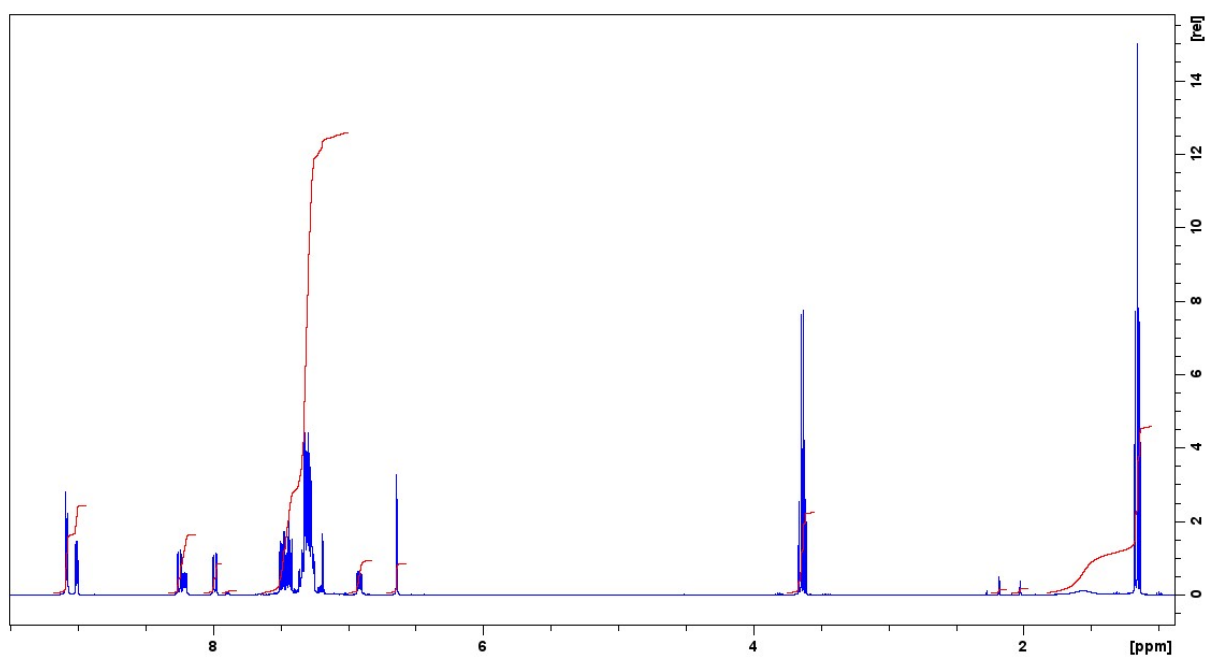


Figure S1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **L1** recorded at 162 MHz in CDCl_3 .



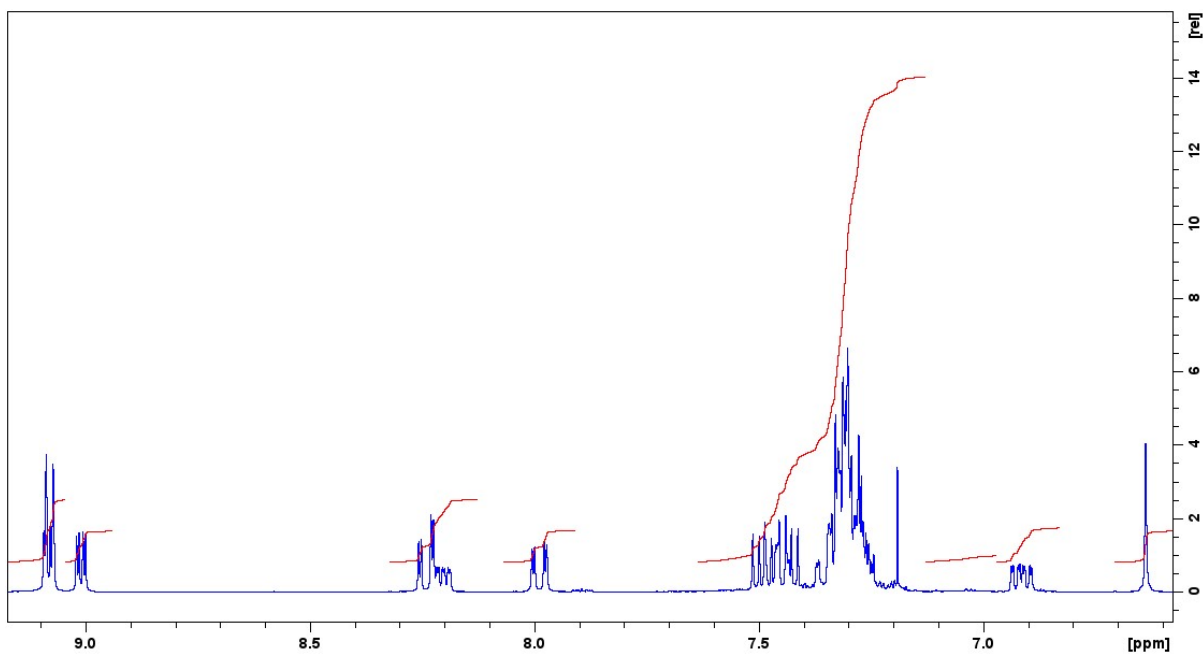


Figure S2 ^1H NMR spectra of **L1** recorded at 400 MHz in CDCl_3 .

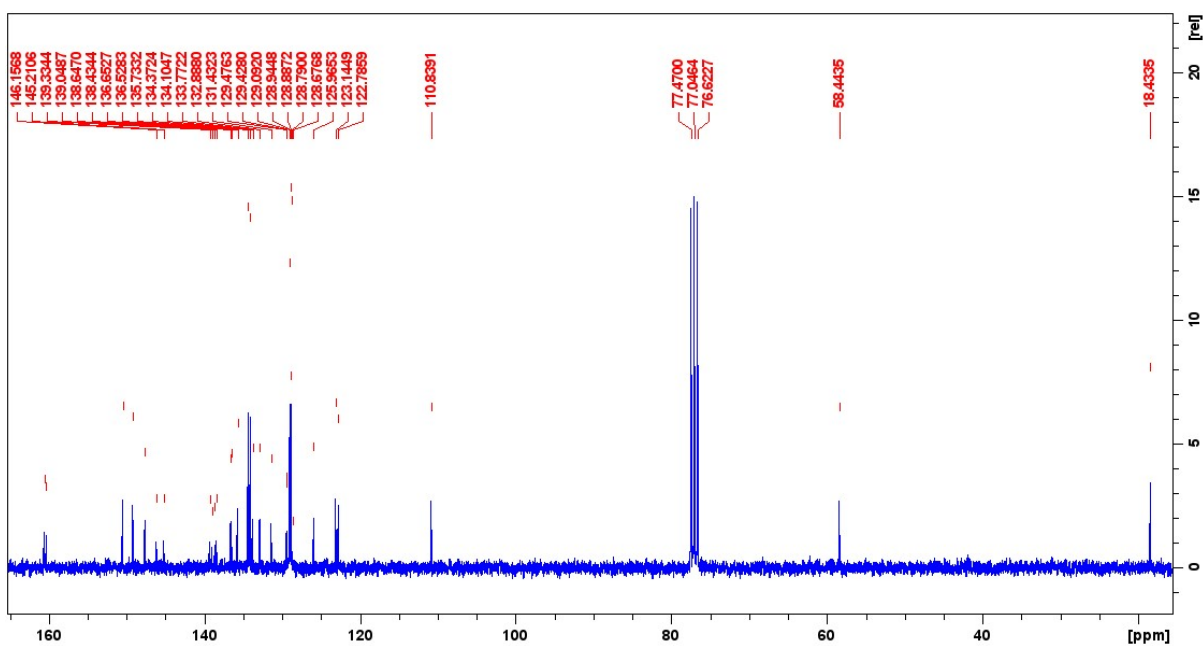


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L1** recorded at 75 MHz in CDCl_3 .

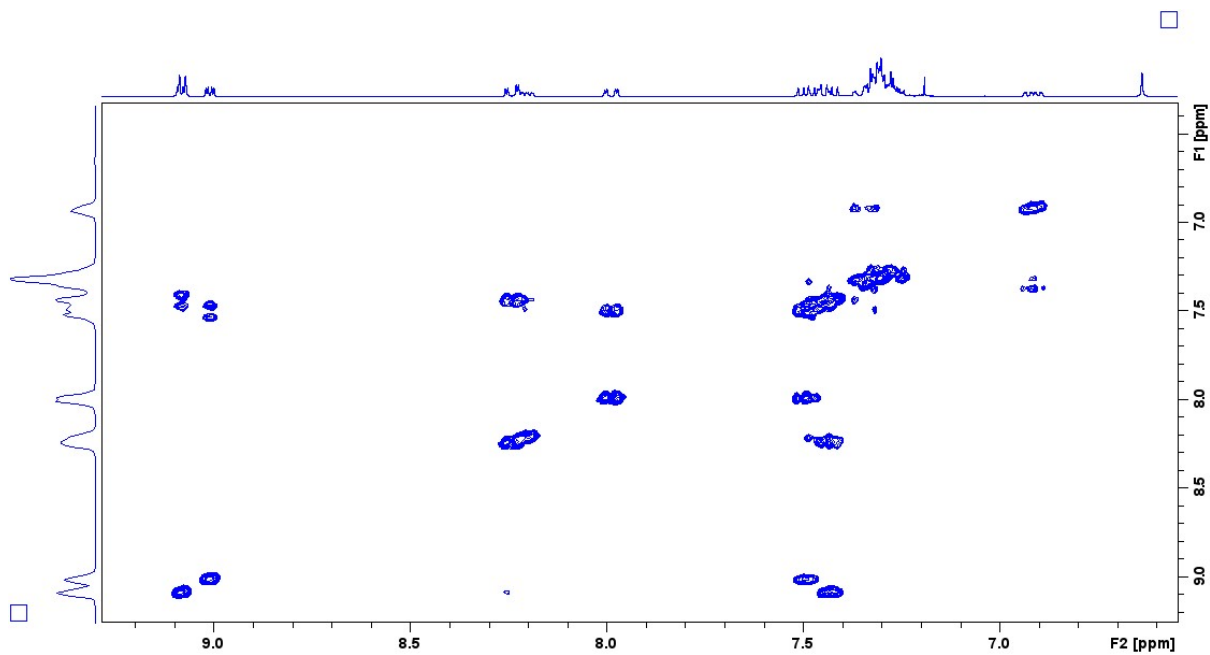


Figure S4. ^1H - ^1H COSY NMR spectrum of **L1** recorded at 400 MHz in CDCl_3 .

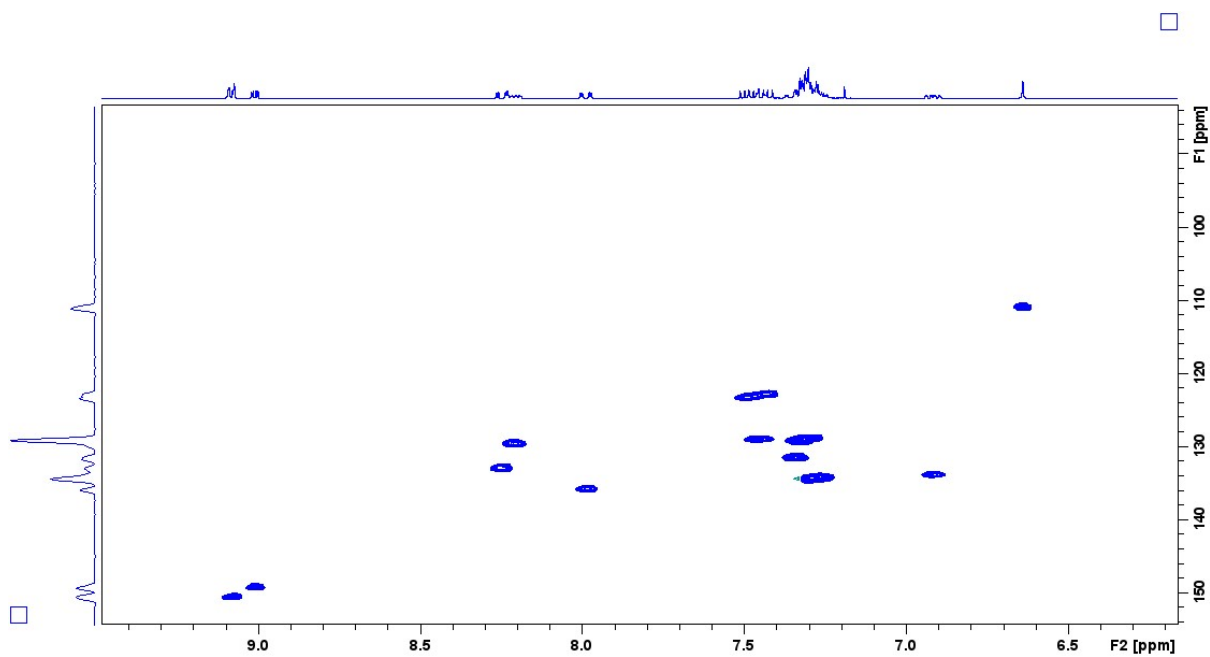


Figure S5. ^1H - ^{13}C HSQC NMR spectrum of **L1** recorded in CDCl_3 .

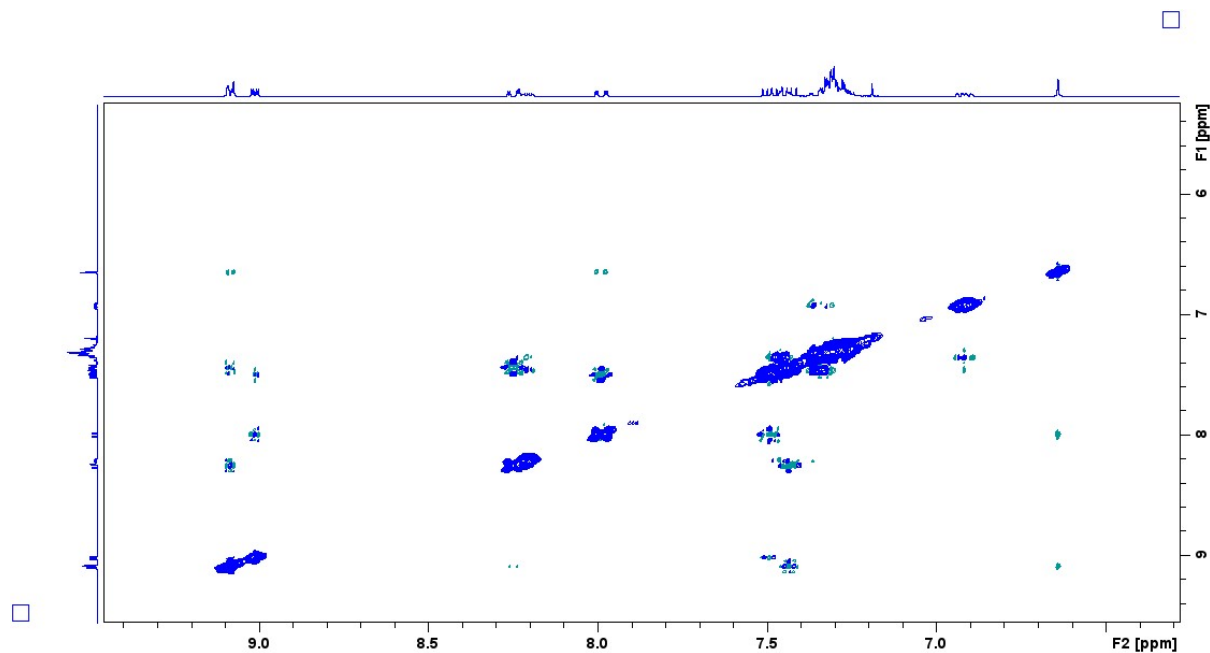
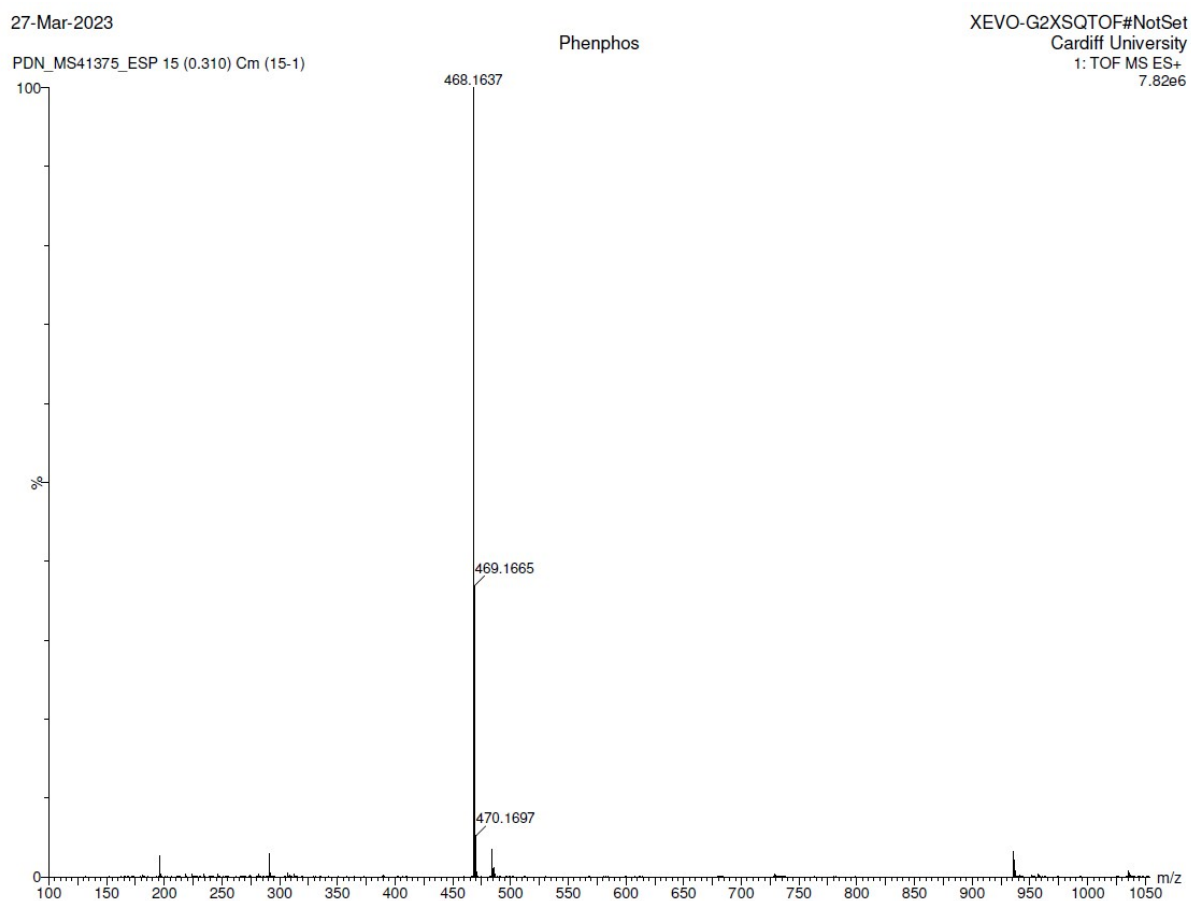


Figure S6. ^1H - ^1H NOESY NMR spectrum of **L1** recorded at 400 MHz in CDCl_3 .



Minimum:				-1.5					
Maximum:	5.0	10.0		100.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula	
468.1637	468.1630	0.7	1.5	22.5	928.4	n/a	n/a	C31 H23 N3 P	

Figure S7. HRMS (ES⁺) spectrum of **L1**.

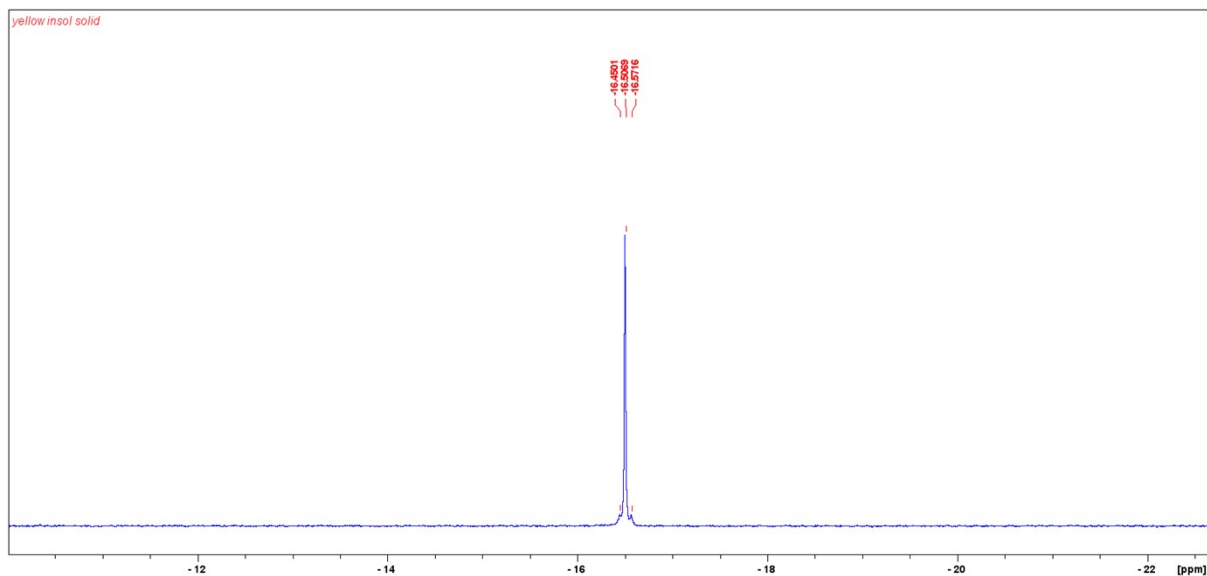


Figure S8. ³¹P{¹H} NMR spectrum of **L2** recorded at 162 MHz in CDCl₃.

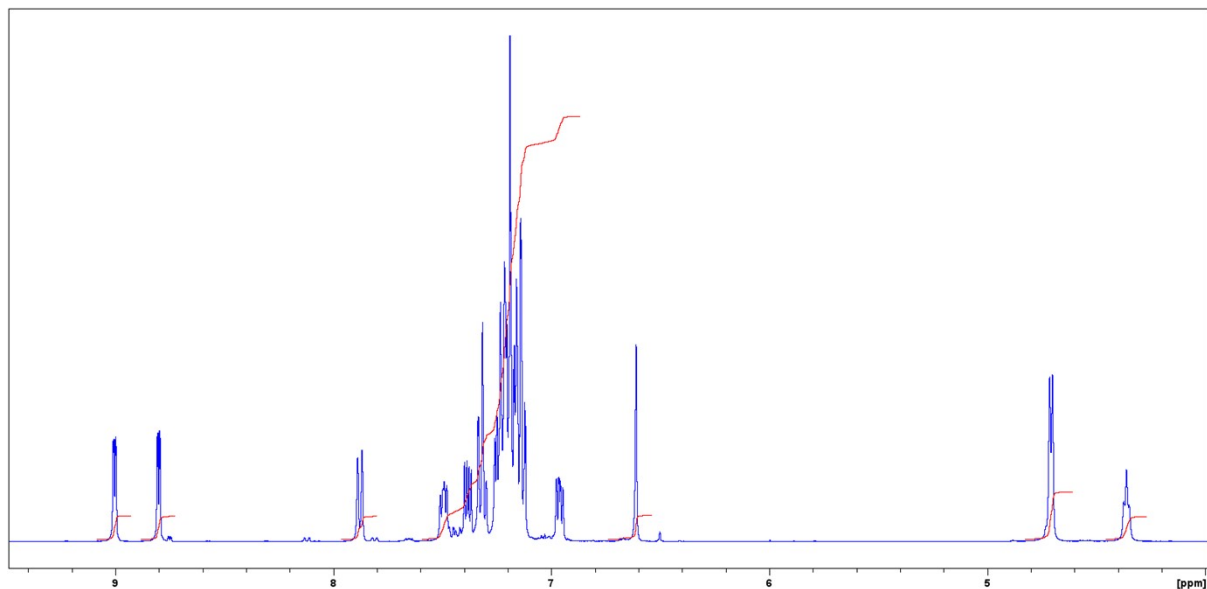


Figure S9 ¹H NMR spectra of **L2** recorded at 400 MHz in CDCl₃.

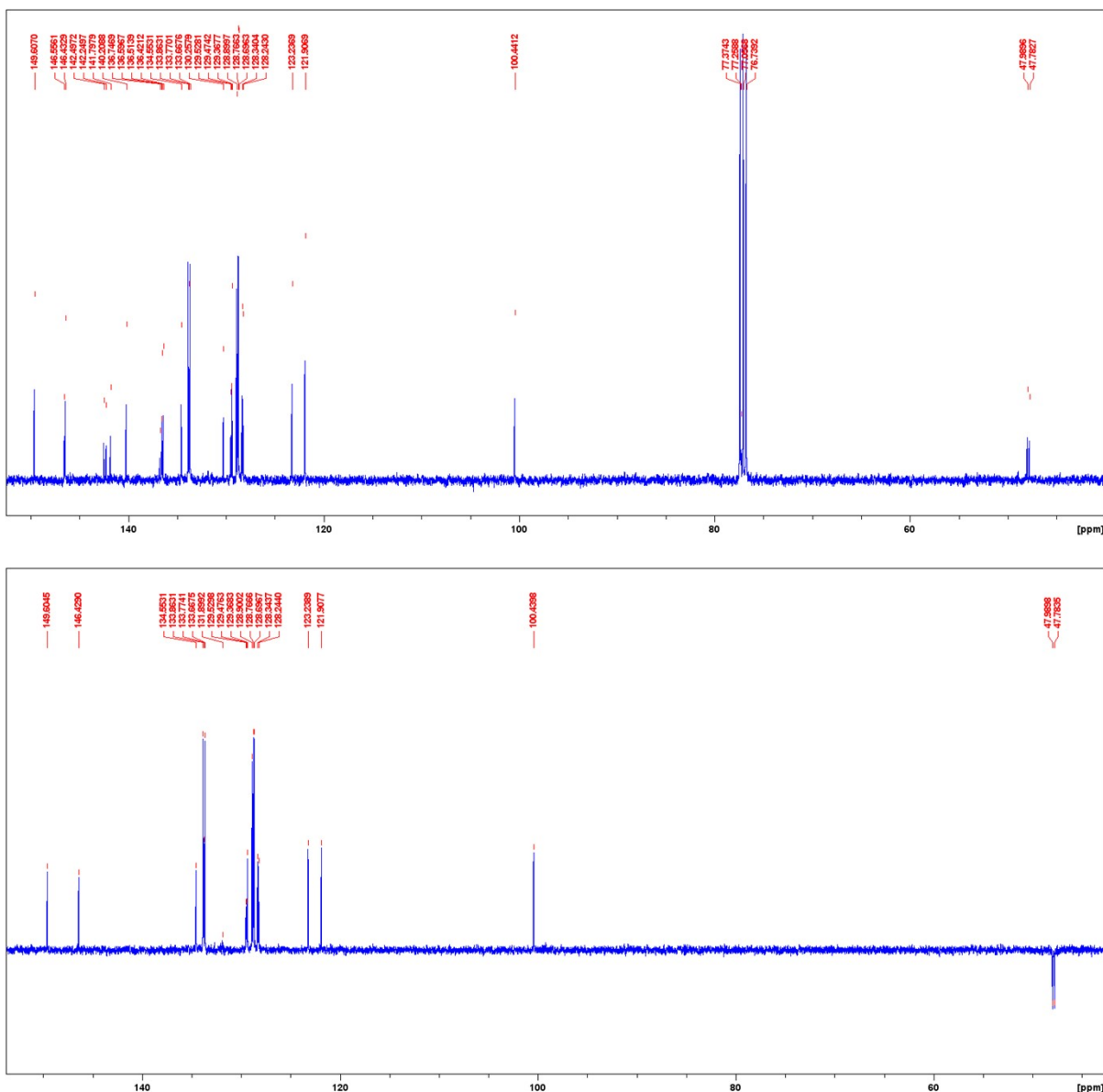


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of L2 recorded at 75 MHz in CDCl_3 .

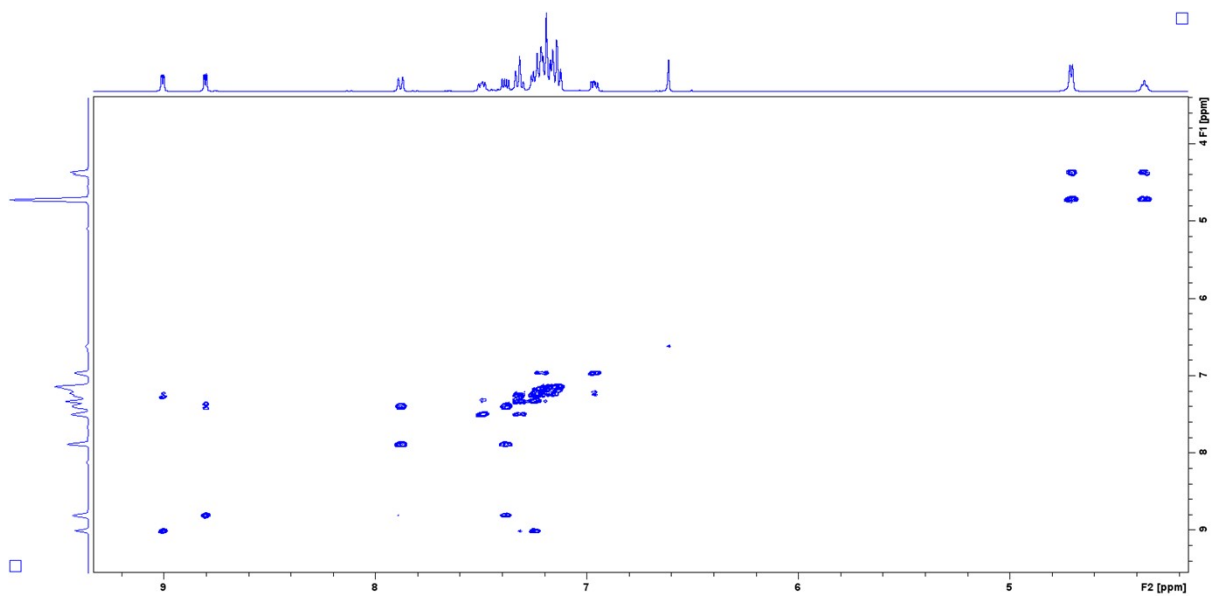


Figure S11. ^1H - ^1H COSY NMR spectrum of **L2** recorded at 400 MHz in CDCl_3 .

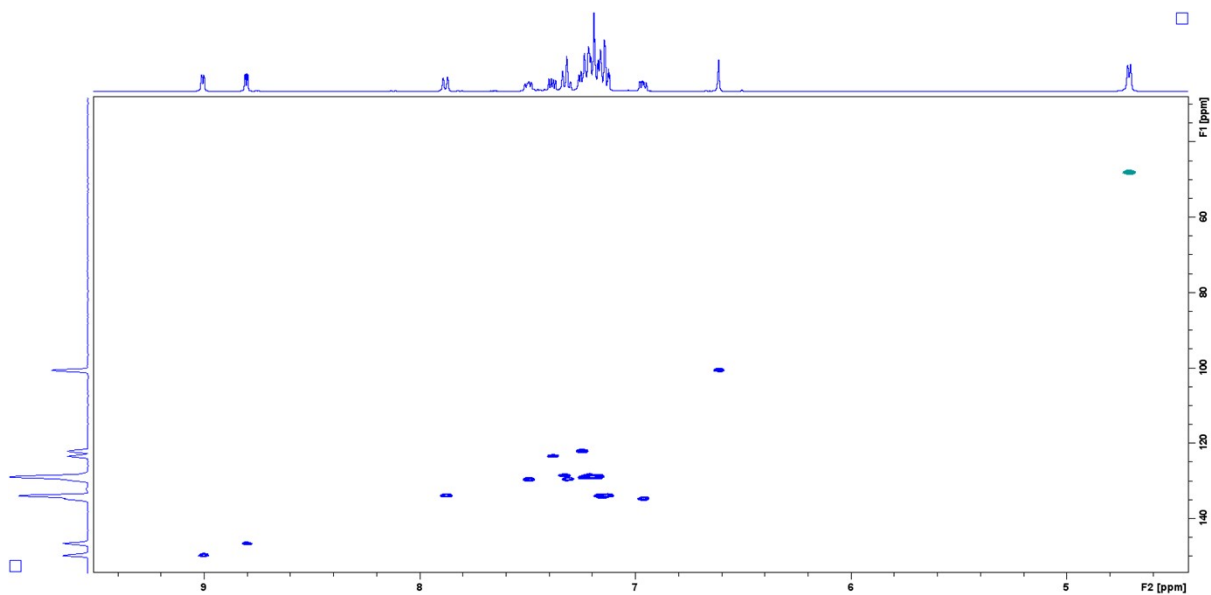


Figure S12. ^1H - ^{13}C HSQC NMR spectrum of **L2** recorded in CDCl_3 .

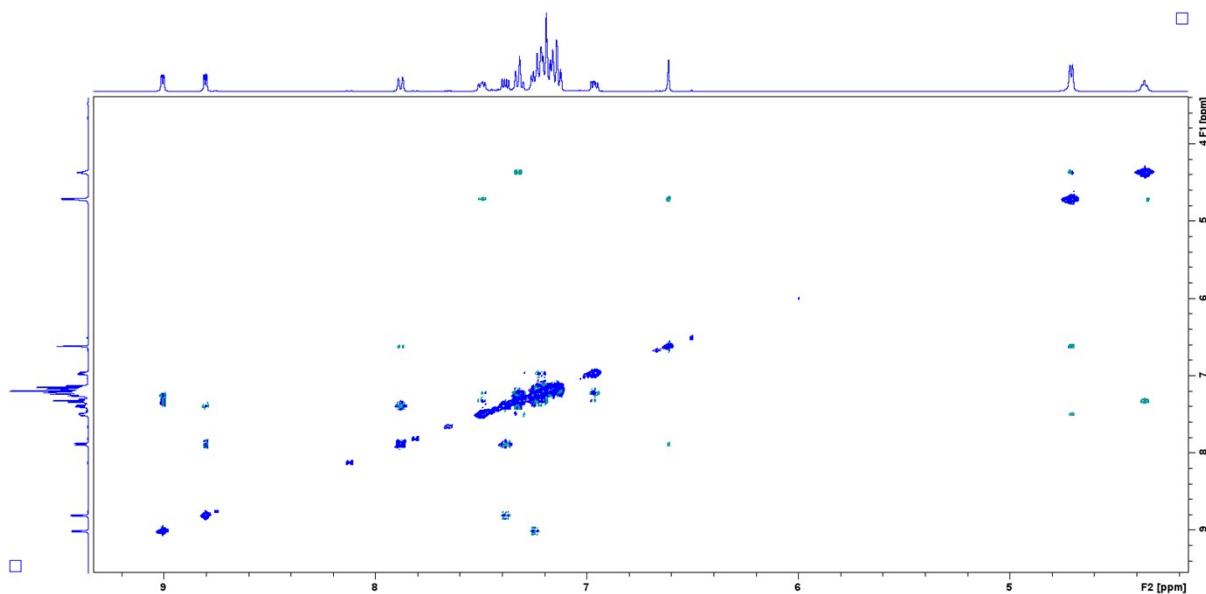
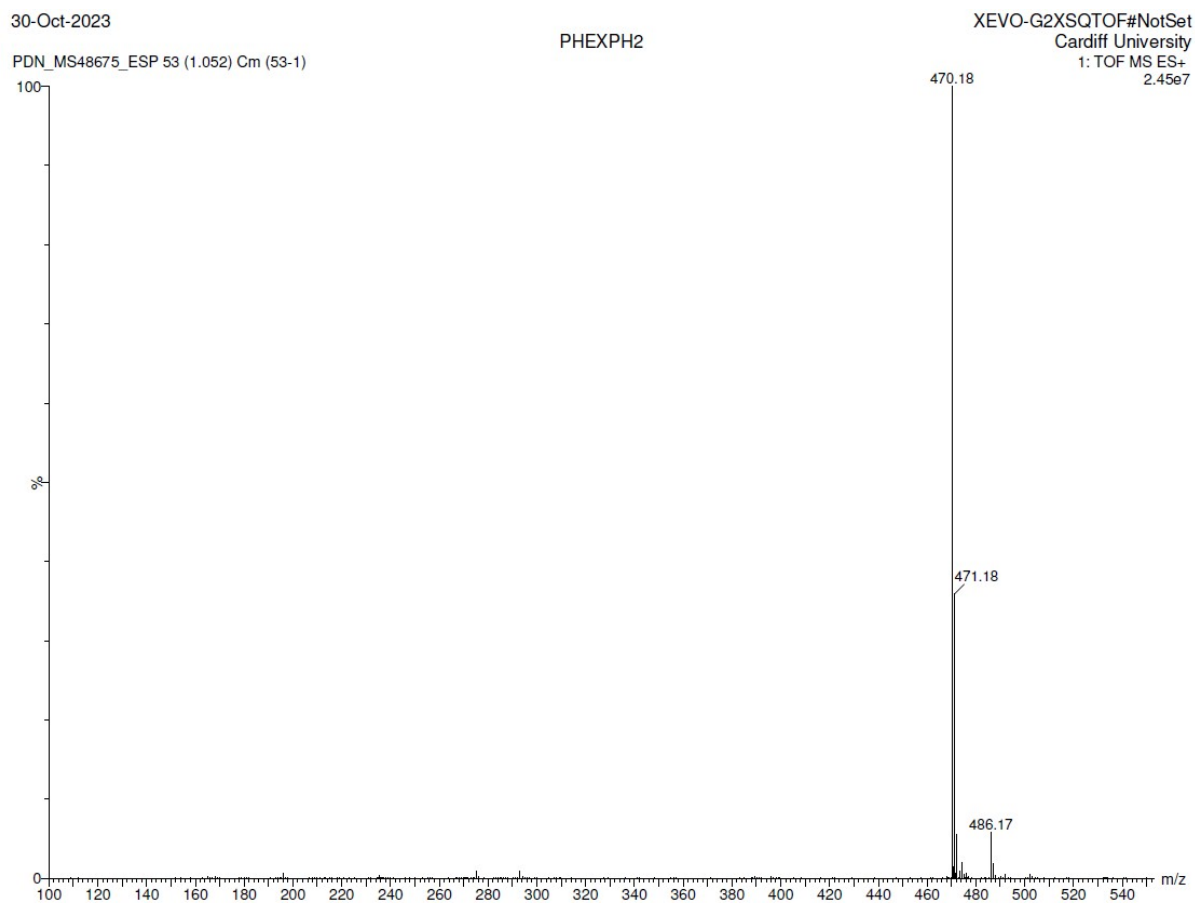


Figure S13. ^1H - ^1H NOESY NMR spectrum of **L2** recorded at 400 MHz in CDCl_3 .



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
470.1791	470.1786	0.5	1.1	21.5	1260.6	n/a	n/a	$\text{C}_{31}\text{H}_{25}\text{N}_3\text{P}$

Figure S14. HRMS (ES^+) spectrum of **L2**.

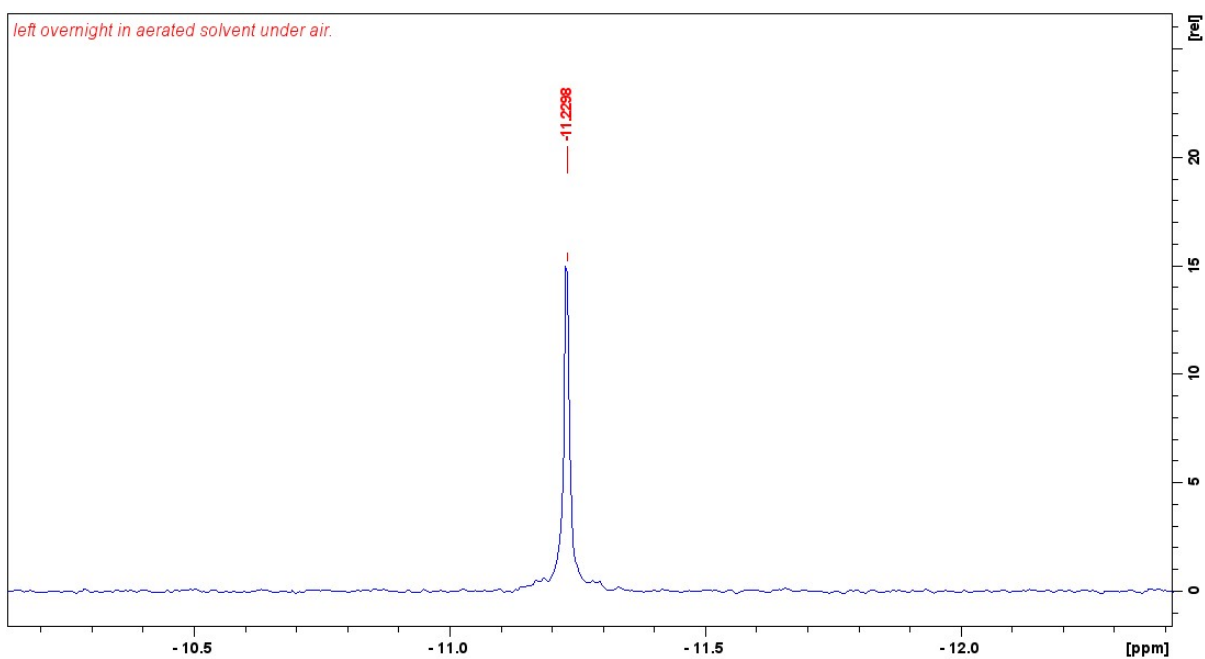


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **RuL1** recorded at 162 MHz in d_6 -dmsd.

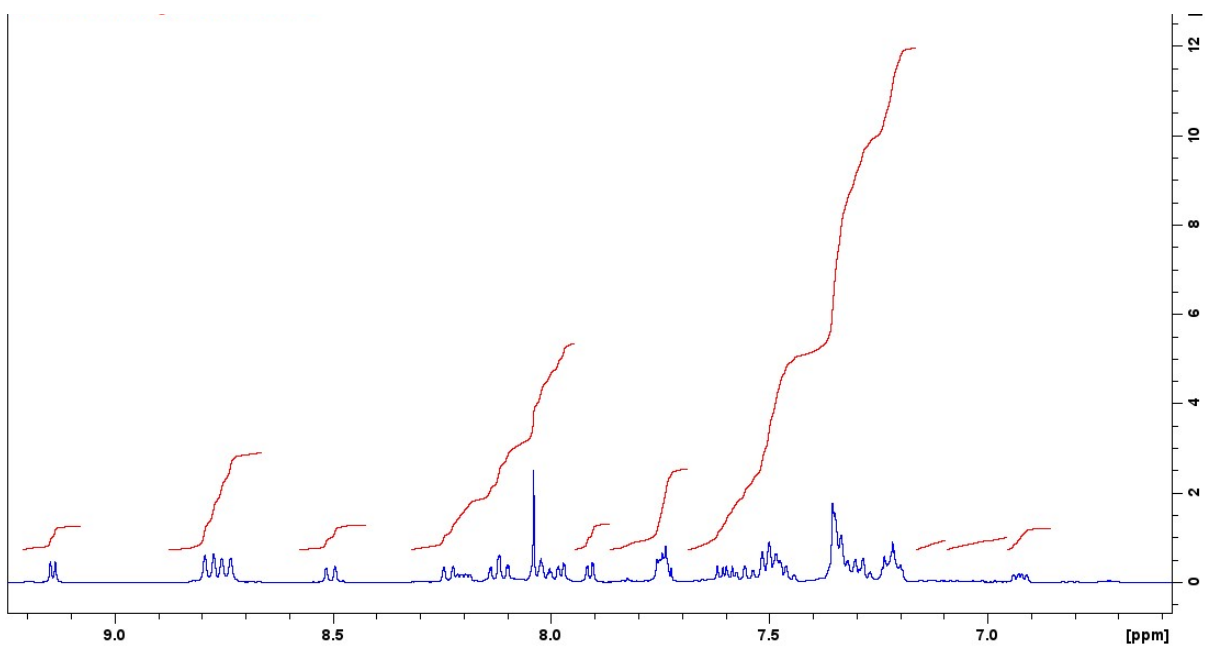


Figure S16 ^1H NMR spectra of **RuL1** recorded at 400 MHz in d_6 -dmsd.

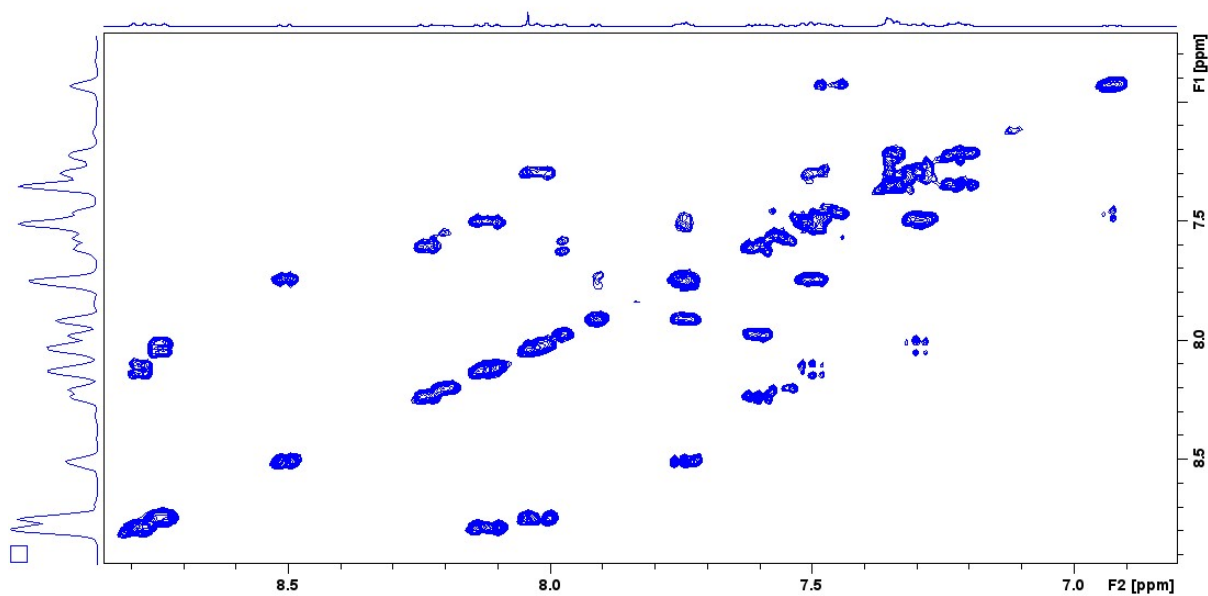


Figure S17. ^1H - ^1H COSY NMR spectrum of **RuL1** recorded at 400 MHz in d_6 -dmsO.

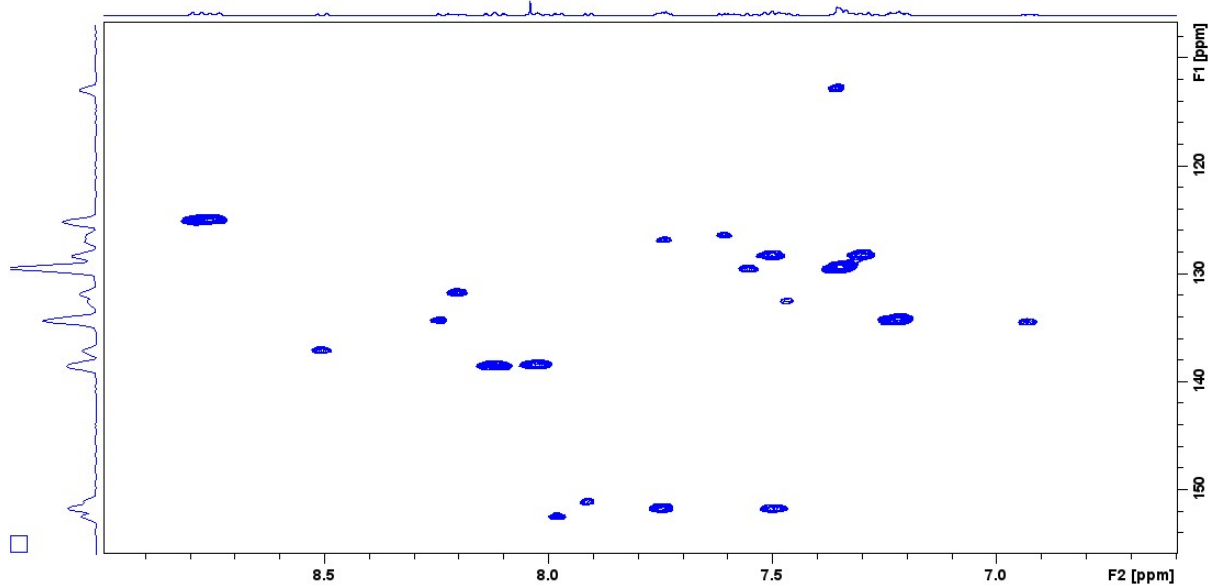


Figure S18. ^1H - ^{13}C HSQC NMR spectrum of **RuL1** recorded in d_6 -dmsO.

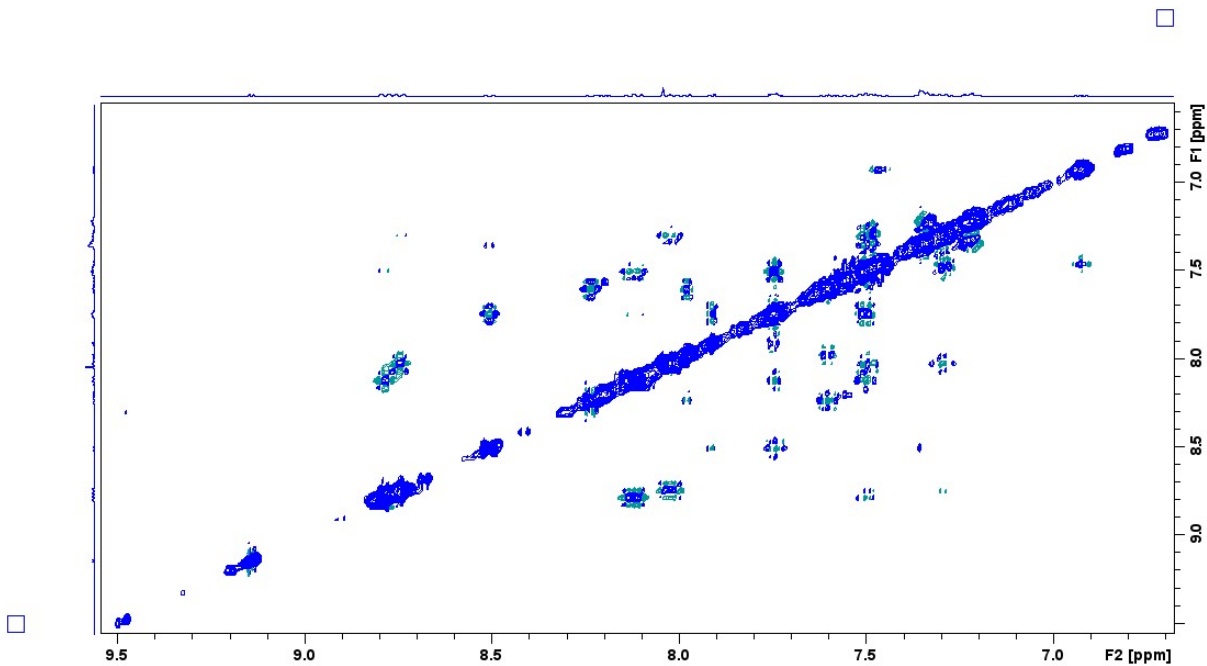


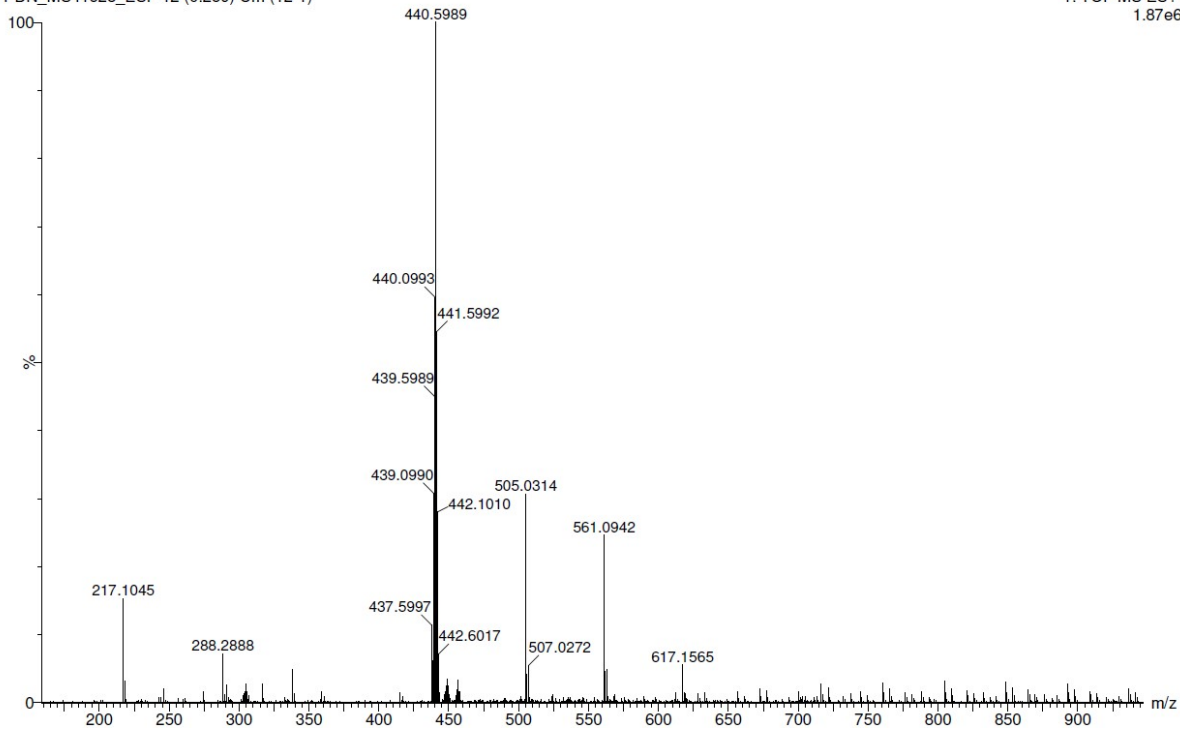
Figure S19. ^1H - ^1H NOESY NMR spectrum of RuL1 recorded at 400 MHz in d_6 -dmsO.

20-Apr-2023

RuphenP

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
1.87e6

PDN_MS41628_ESP 12 (0.259) Cm (12-1)

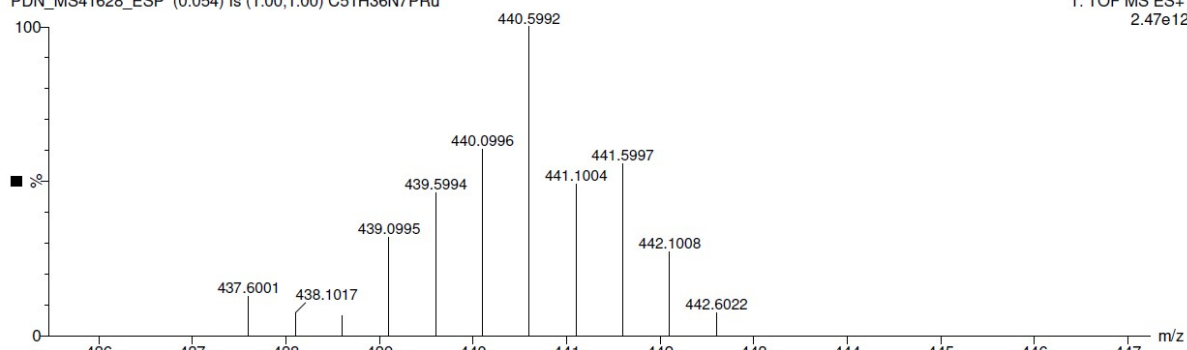


20-Apr-2023

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
2.47e12

PDN_MS41628_ESP (0.054) Is (1.00,1.00) C₅₁H₃₆N₇PRu

RuphenP



PDN_MS41628_ESP 12 (0.259) Cm (12-1)

1: TOF MS ES+
1.87e6

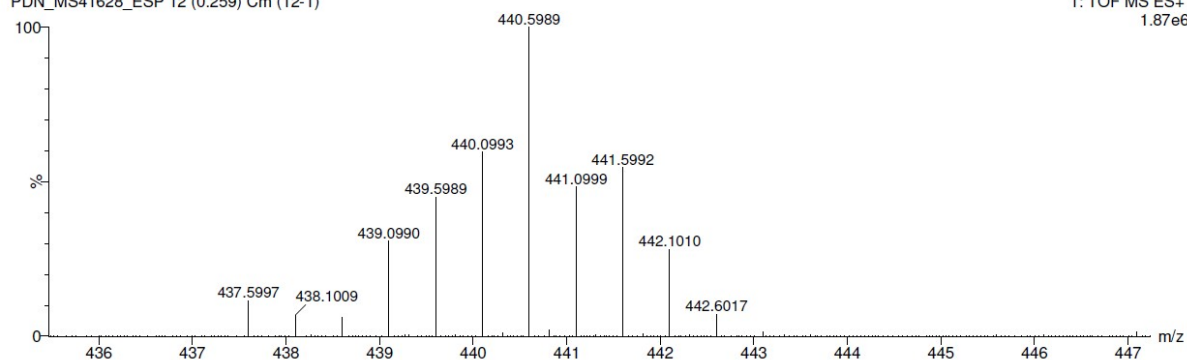


Figure S20. HRMS (ES⁺) spectrum of **RuL1**.

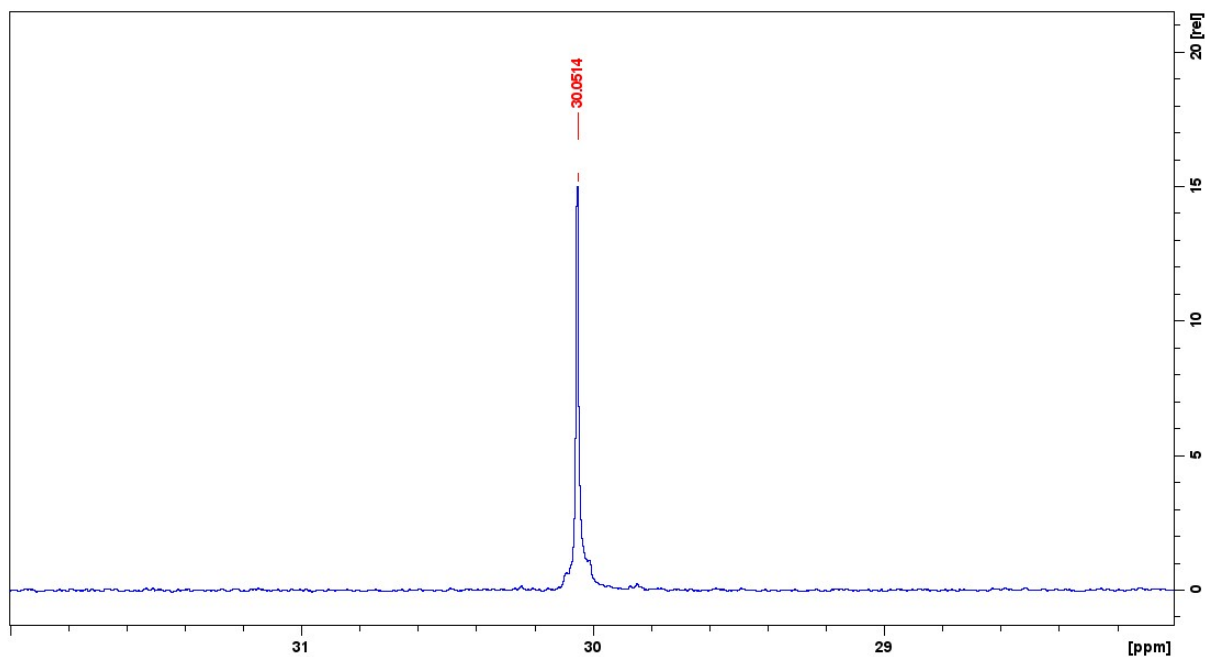


Figure S21. ³¹P{¹H} NMR spectrum of **RuAuL1** recorded at 162 MHz in d₆-dmsO.

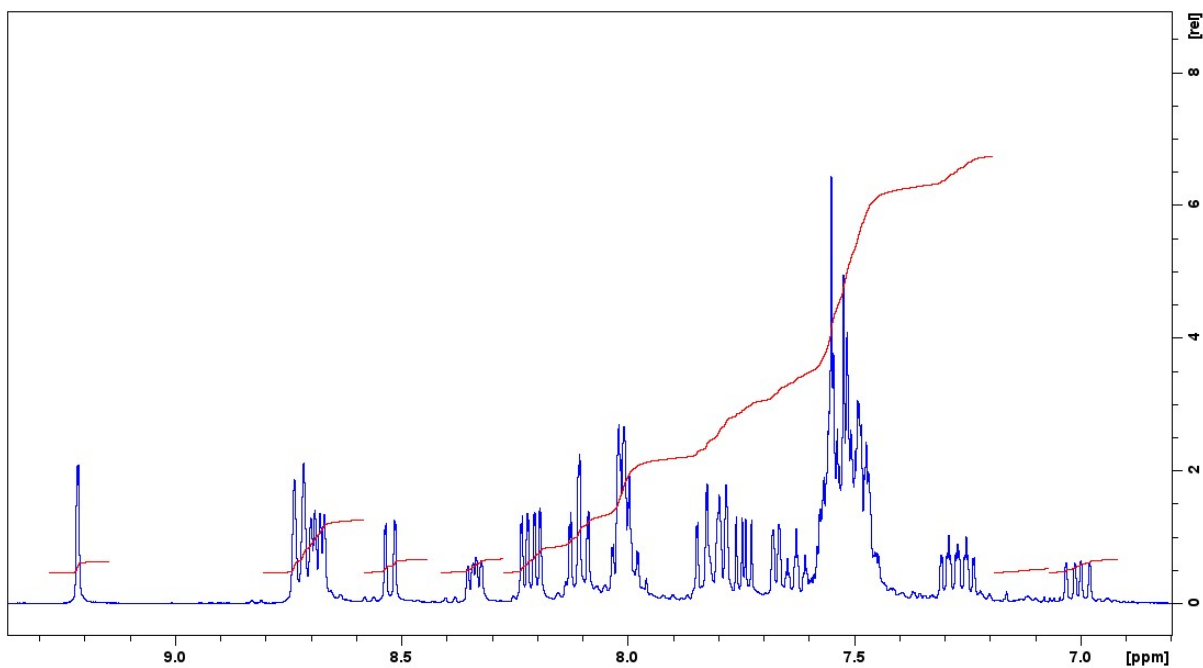
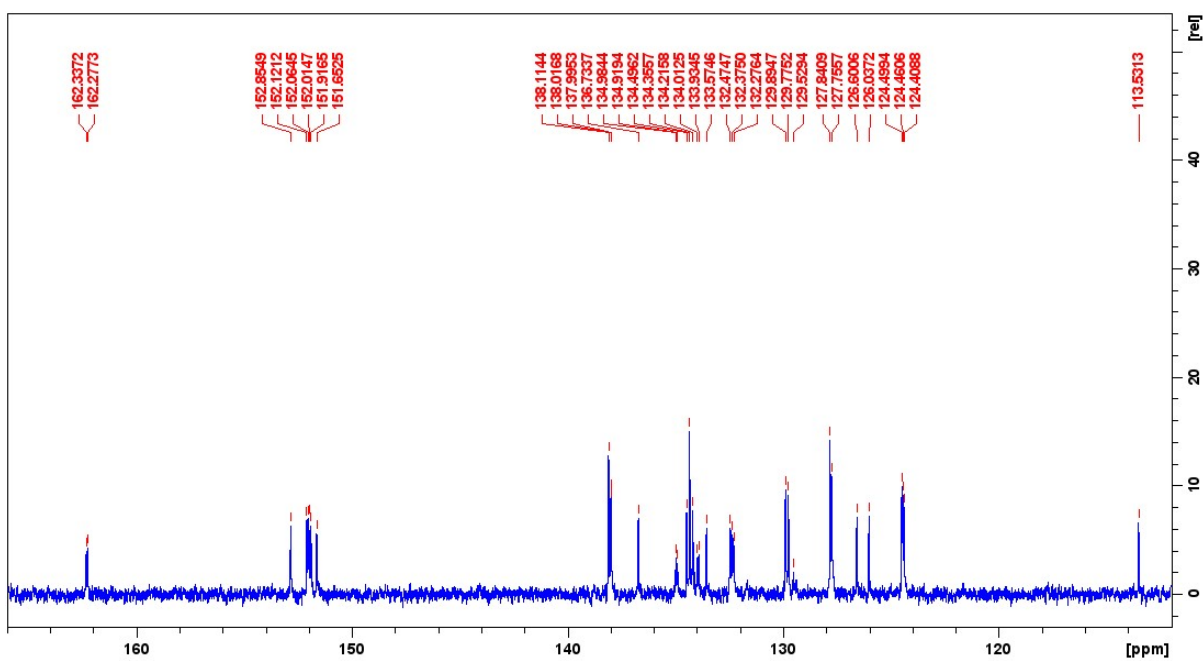


Figure S22 ^1H NMR spectra of RuAuL1 recorded at 400 MHz in d_6 -dmsO.



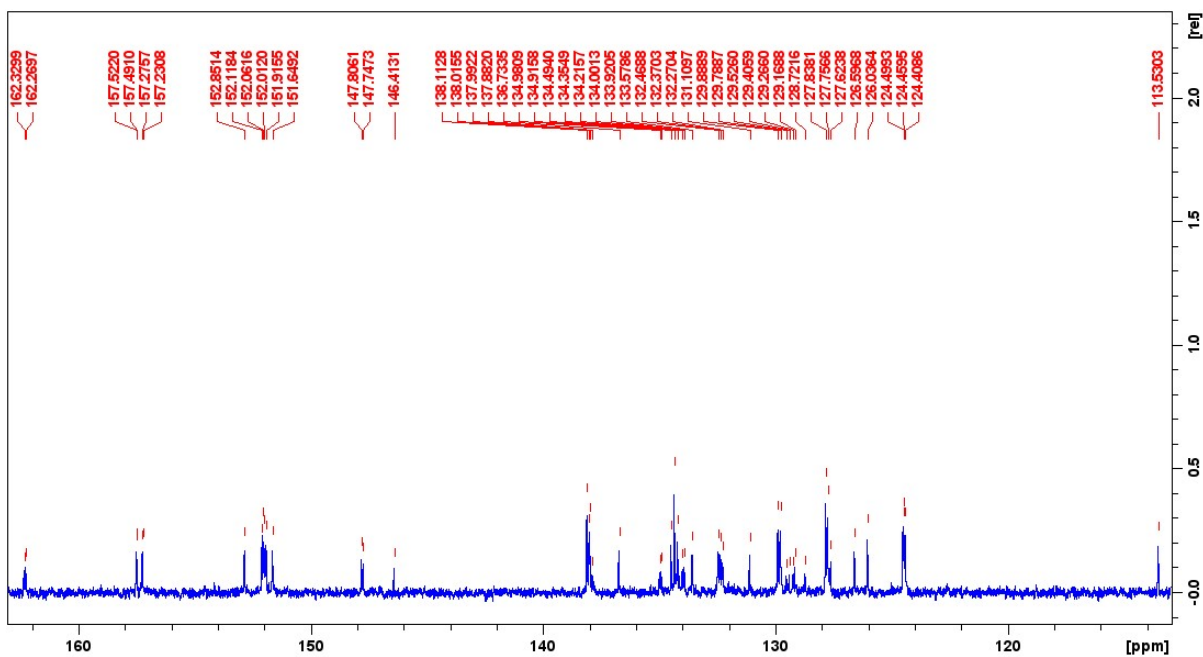


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **RuAuL1** recorded at 75 MHz in d_6 -dmsO.

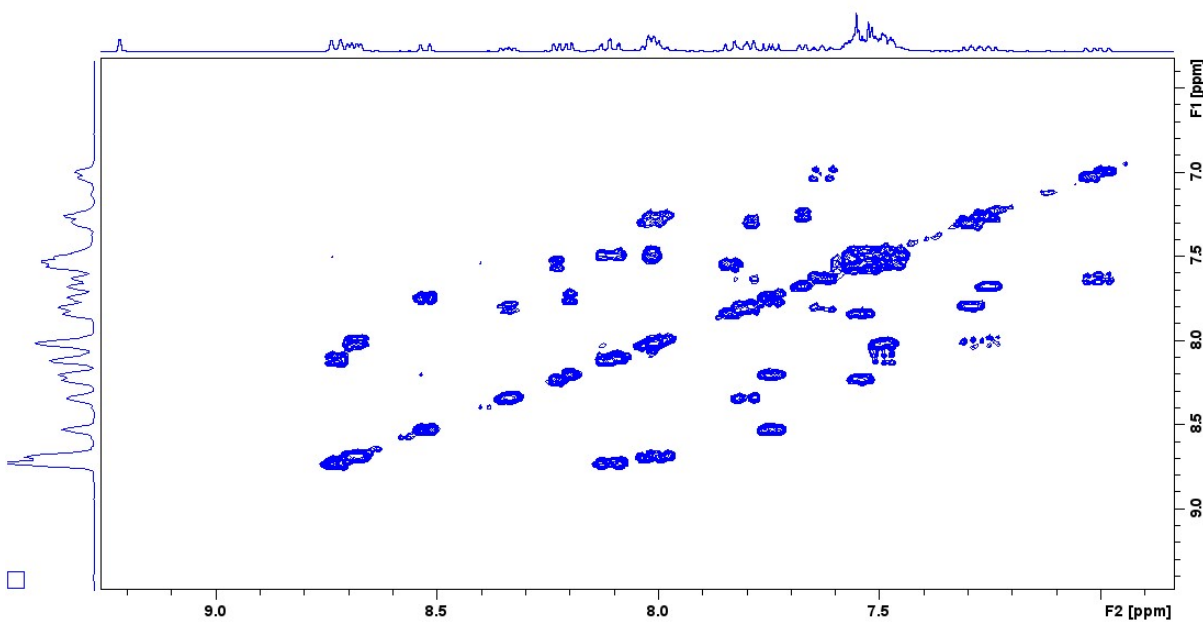


Figure S24. ^1H - ^1H COSY NMR spectrum of **RuAuL1** recorded at 400 MHz in d_6 -dmsO.

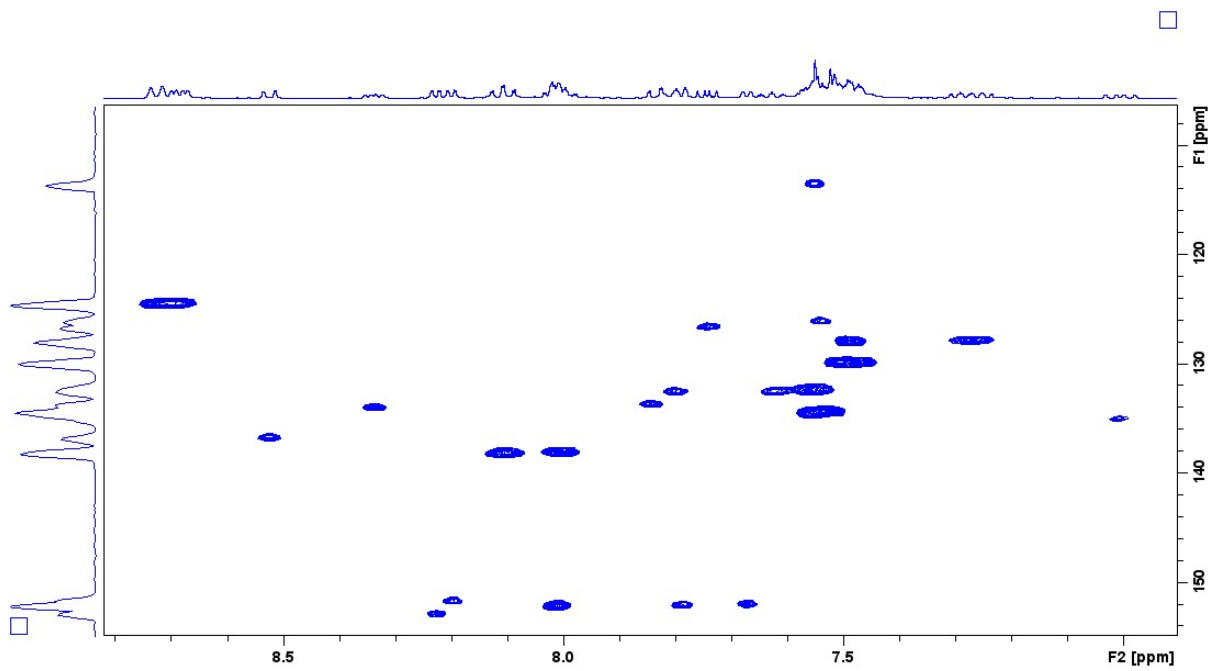


Figure S25. ^1H - ^{13}C HSQC NMR spectrum of RuAuL1 recorded in d_6 -dmsO.

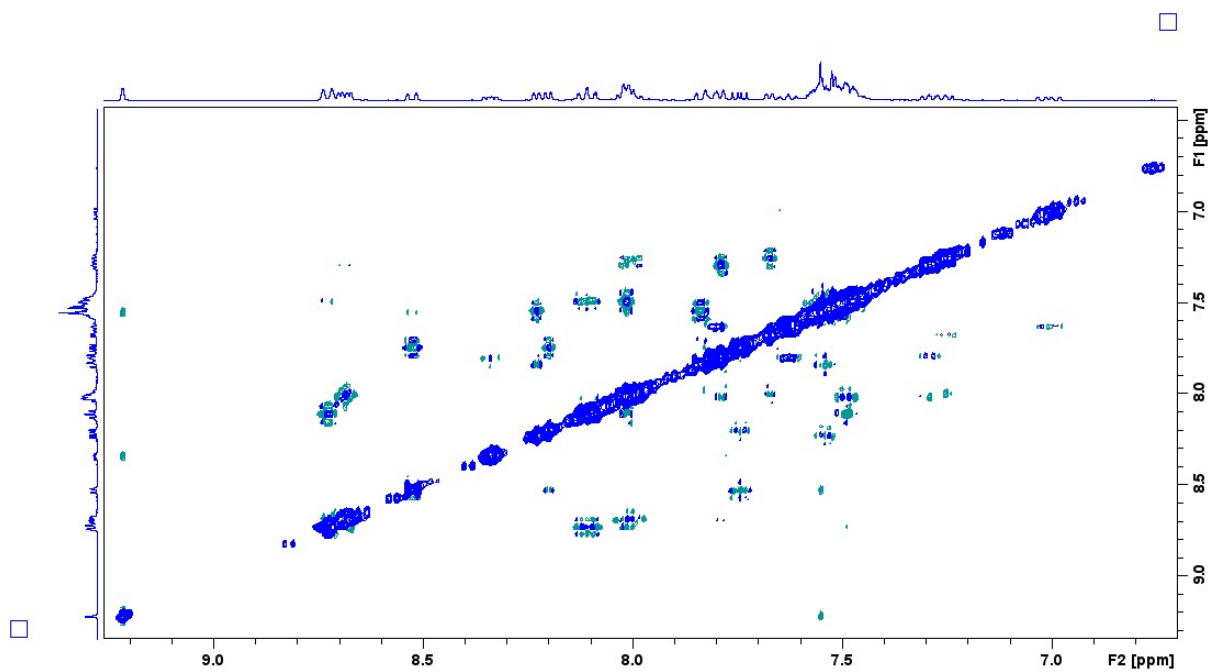


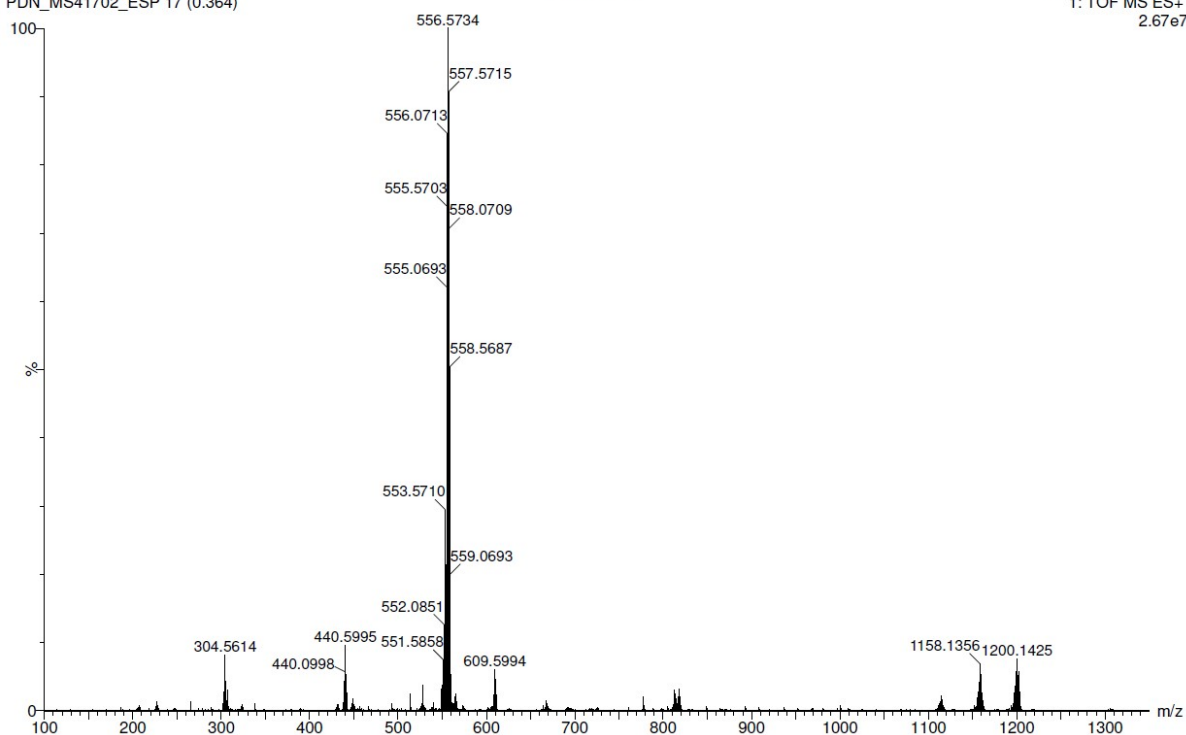
Figure S26. ^1H - ^1H NOESY NMR spectrum of RuAuL1 recorded at 400 MHz in d_6 -dmsO.

28-Apr-2023

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
2.67e7

PDN_MS41702_ESP 17 (0.364)

RuphenAu



Minimum: -1.5
Maximum: 5.0 10.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1200.1371	1200.1353	1.8	1.5	35.5	766.9	n/a	n/a	C51 H38 B N7 F4 P Cl 102Ru 197Au

Figure S27. HRMS (ES⁺) spectrum of RuAuL1.

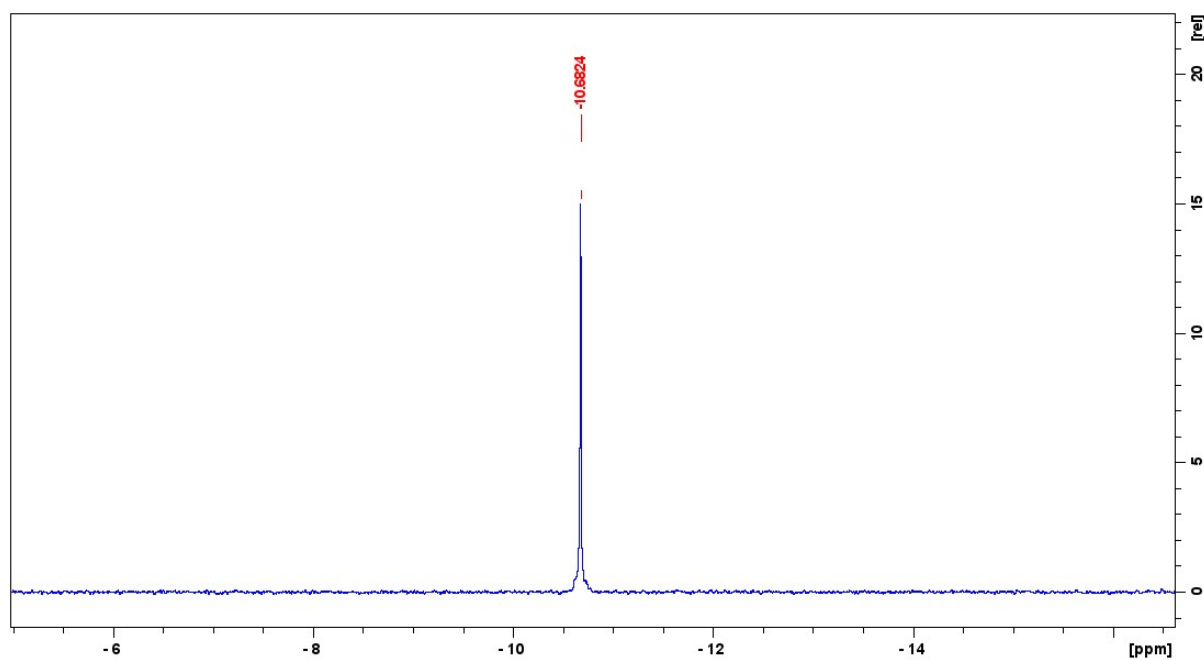


Figure S28. ³¹P{¹H} NMR spectrum of ReL1 recorded at 162 MHz in CDCl₃.

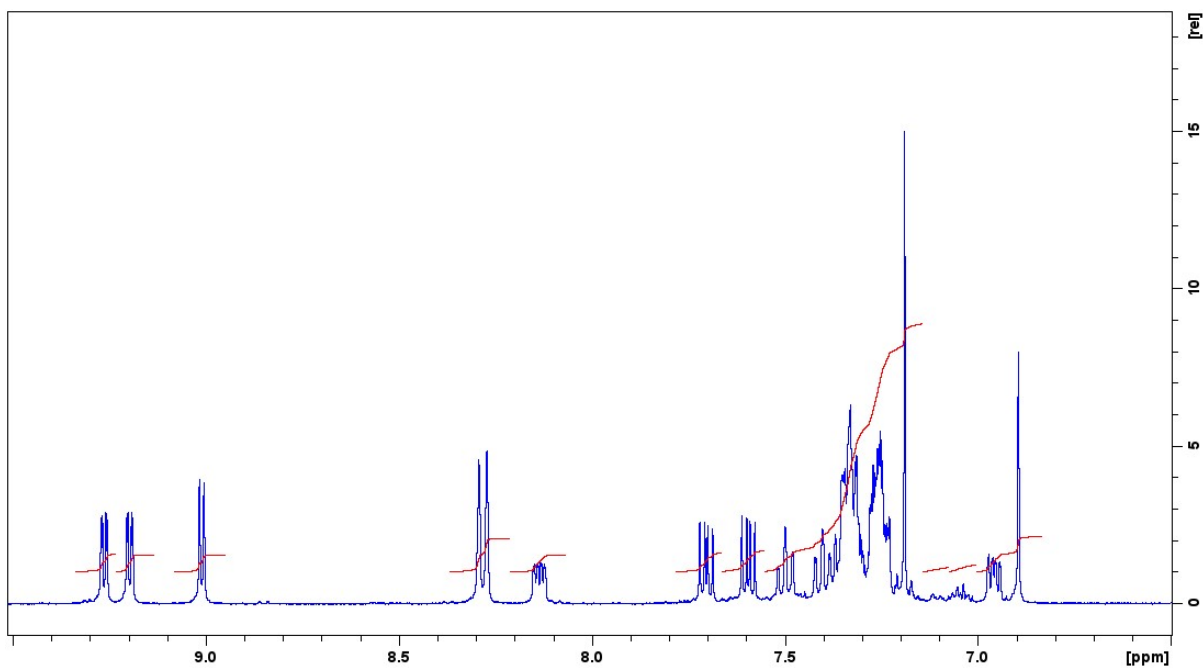
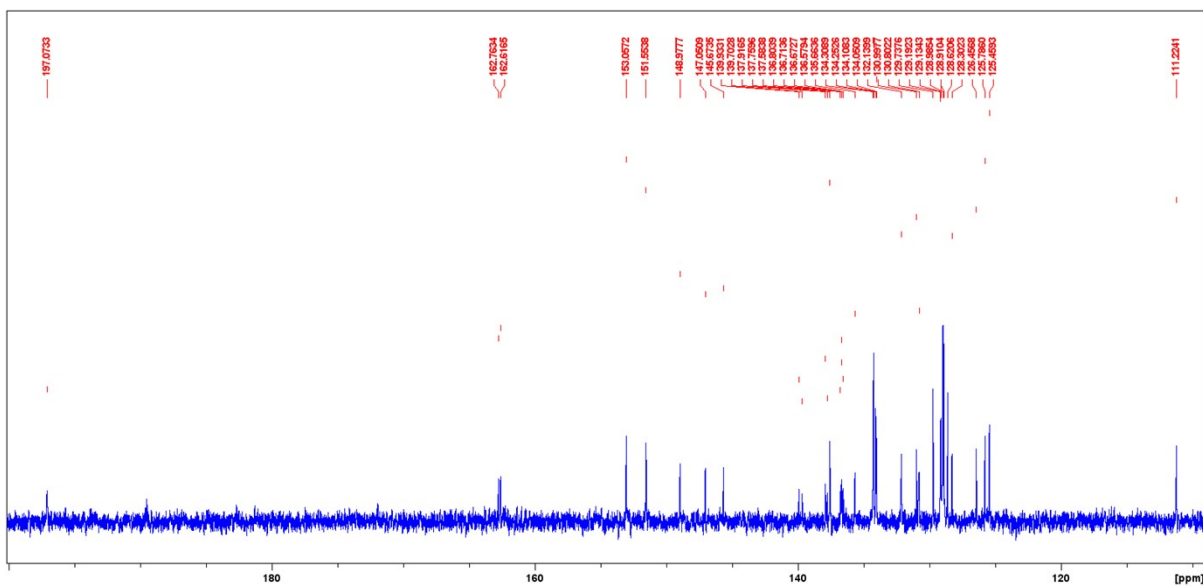


Figure S29 ^1H NMR spectra of ReL1 recorded at 400 MHz in CDCl_3 .



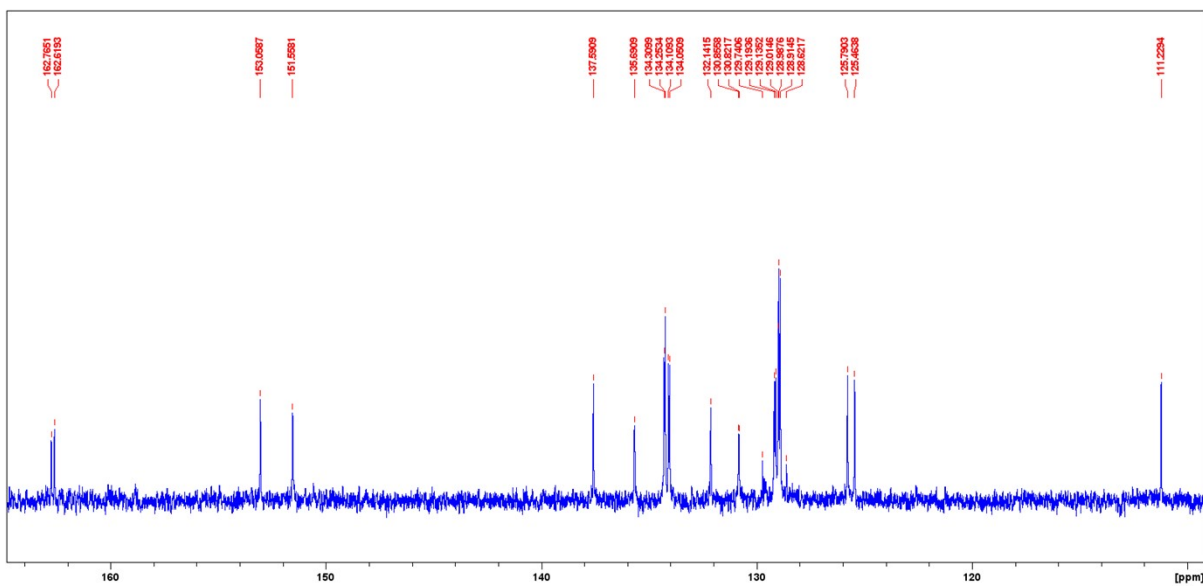


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **ReL1** recorded at 75 MHz in CDCl_3 .

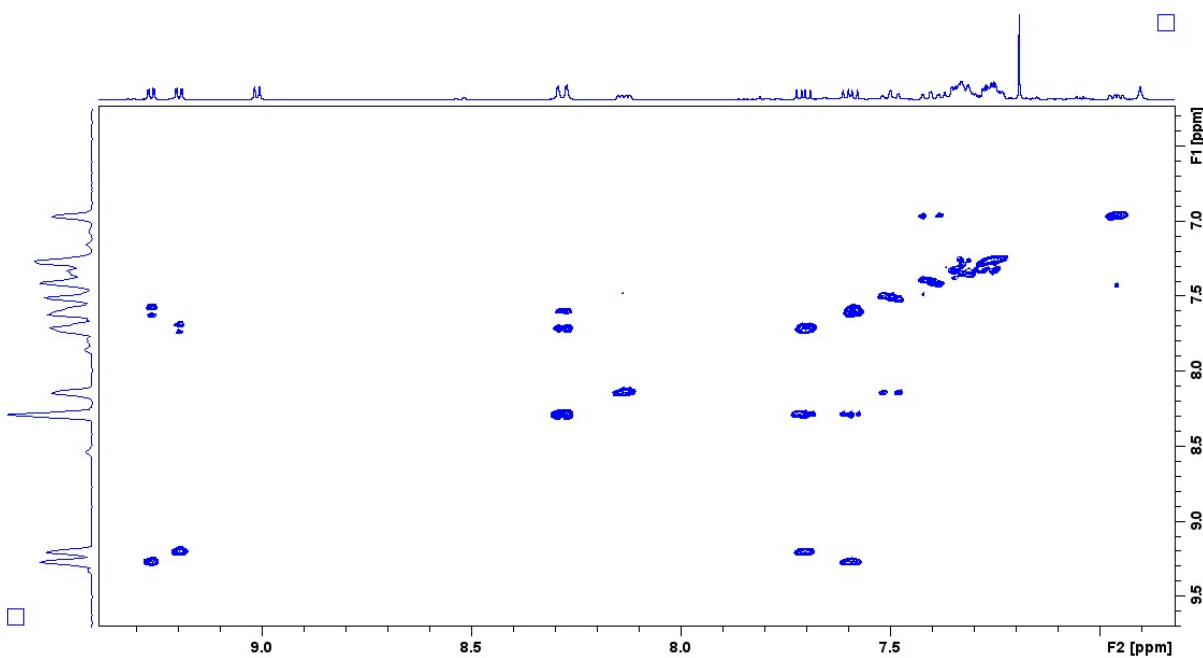


Figure S31. ^1H - ^1H COSY NMR spectrum of **ReL1** recorded at 400 MHz in CDCl_3 .

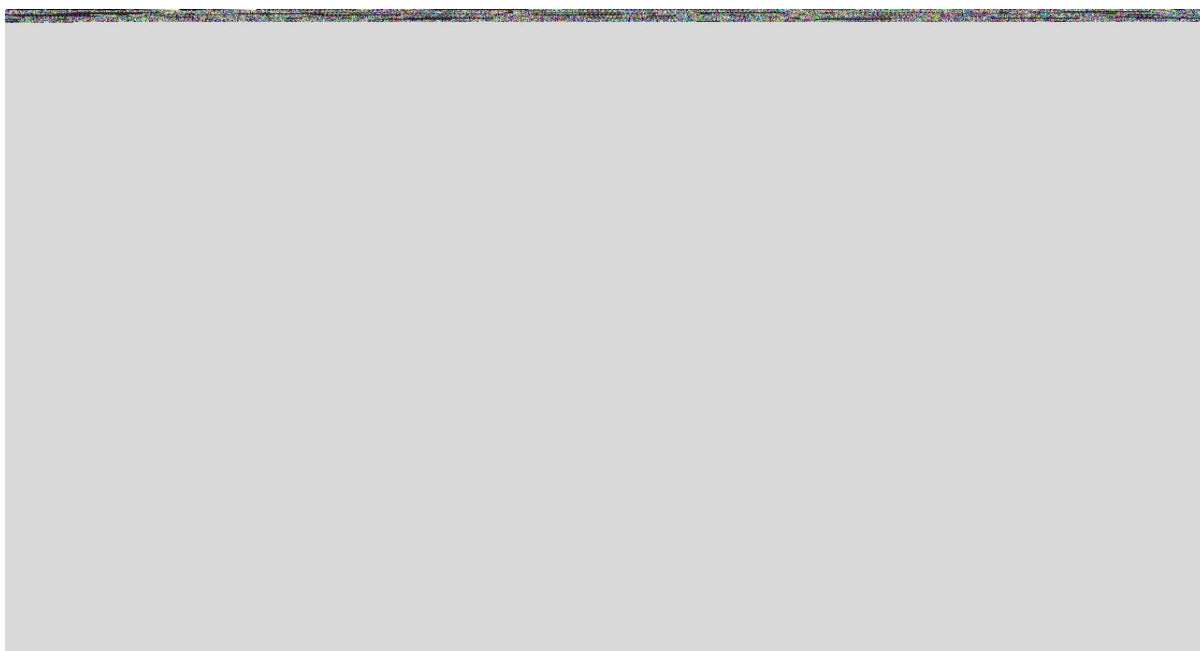


Figure S32. ^1H - ^{13}C HSQC NMR spectrum of **ReL1** recorded in CDCl_3 .

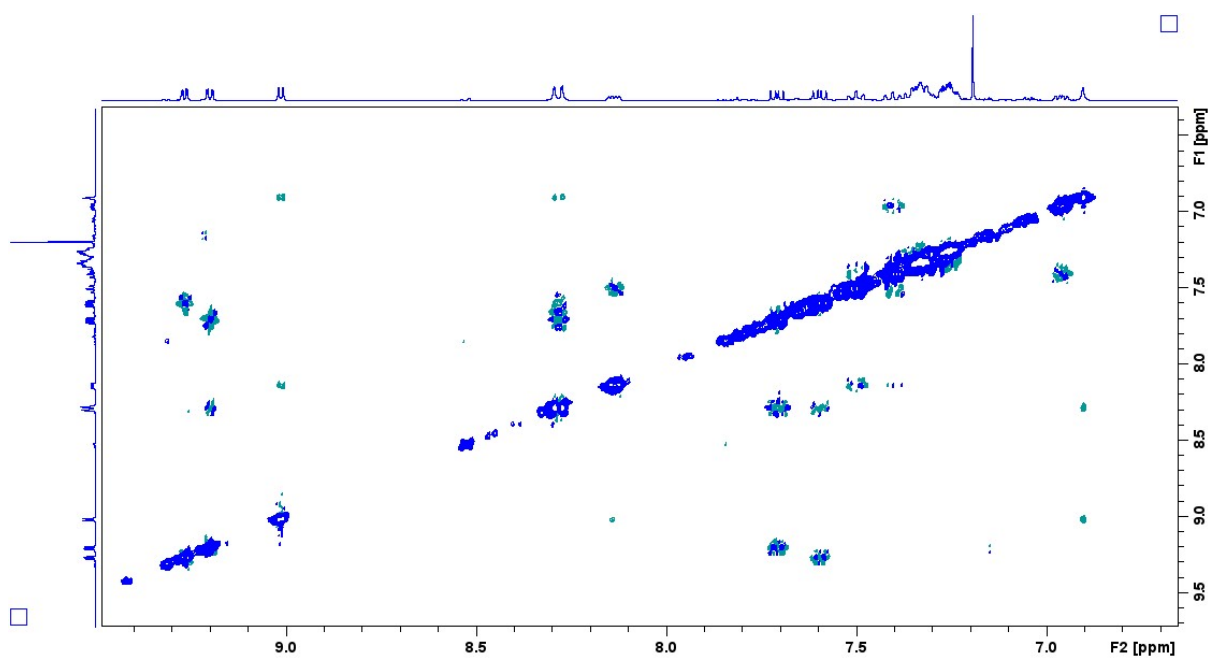


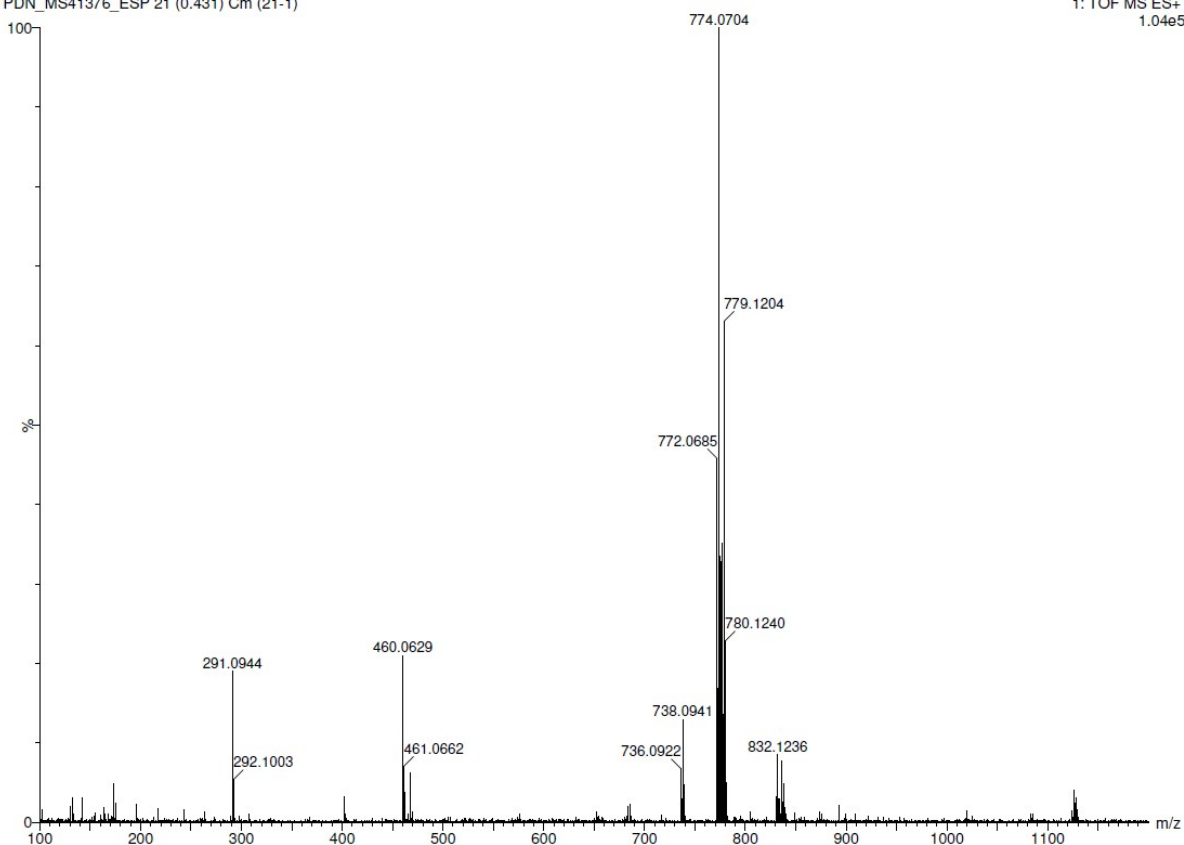
Figure S33. ^1H - ^1H NOESY NMR spectrum of **ReL1** recorded at 400 MHz in CDCl_3 .

27-Mar-2023

PDN_MS41376_ESP 21 (0.431) Cm (21-1)

RePhenP

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
1.04e5



Minimum: -1.5
Maximum: 5.0 10.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
774.0706	774.0693	1.3	1.7	19.5	322.5	n/a	n/a	C27 H20 N3 O 185Re 187Re

Figure S34. HRMS (ES⁺) spectrum of ReL1.

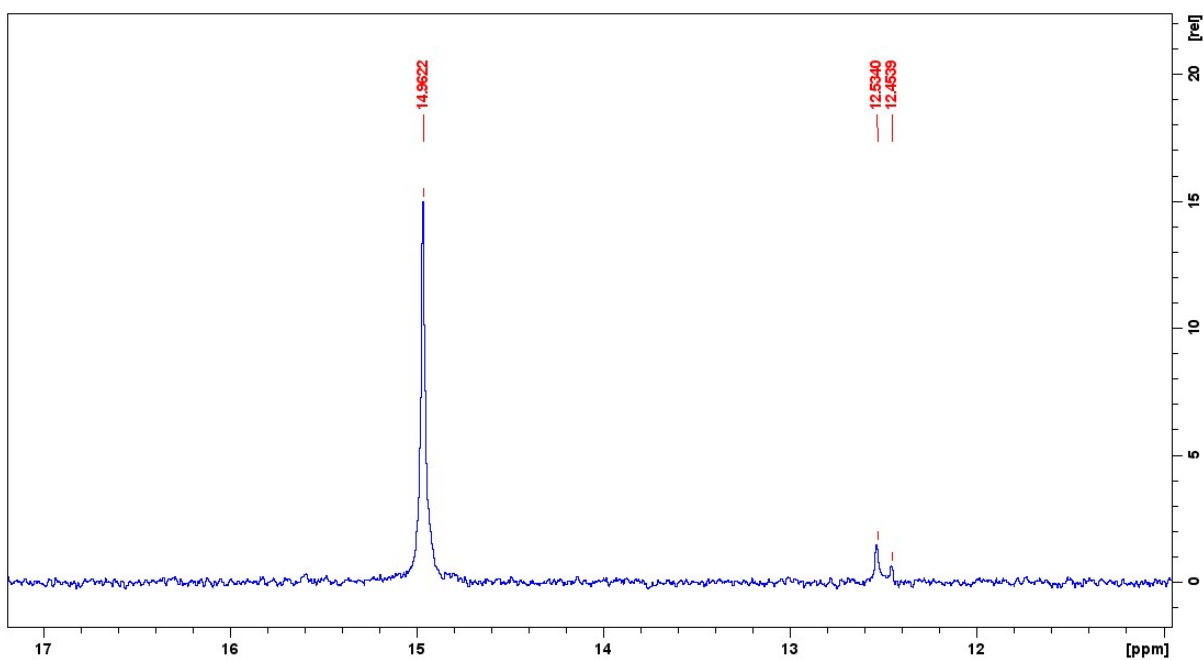


Figure S35. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2ReL1** recorded at 162 MHz in d_6 -acetone.

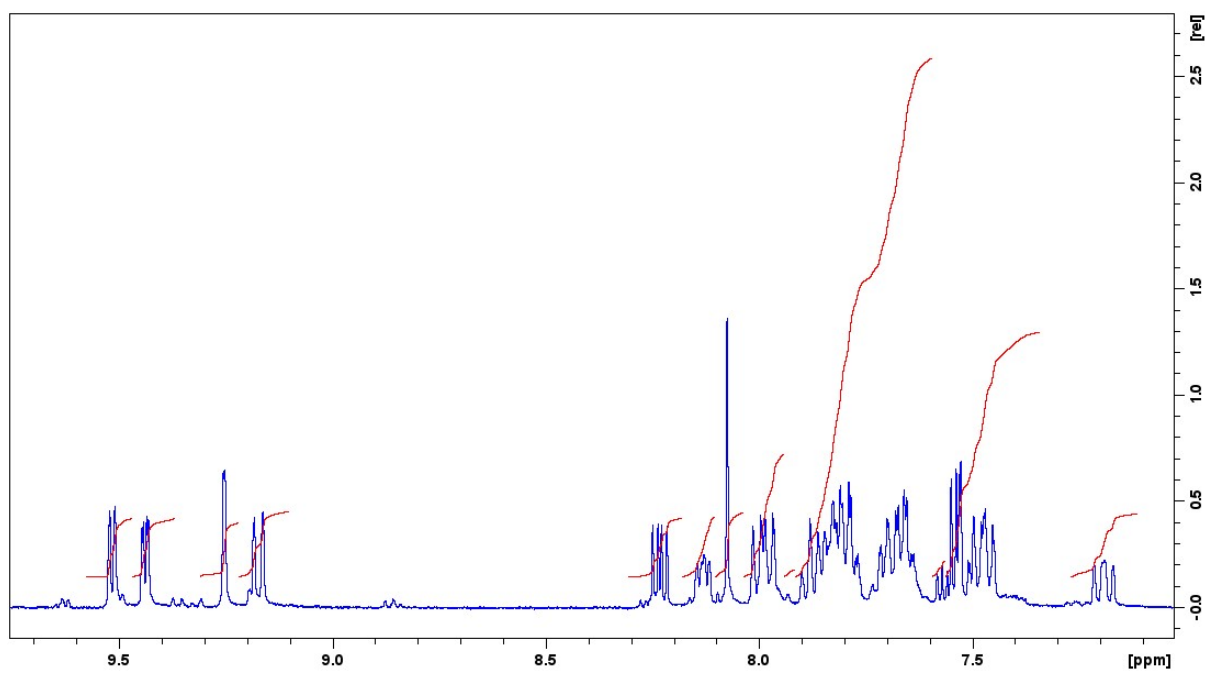


Figure S36. ^1H NMR spectra of **2ReL1** recorded at 400 MHz in d_6 -acetone.

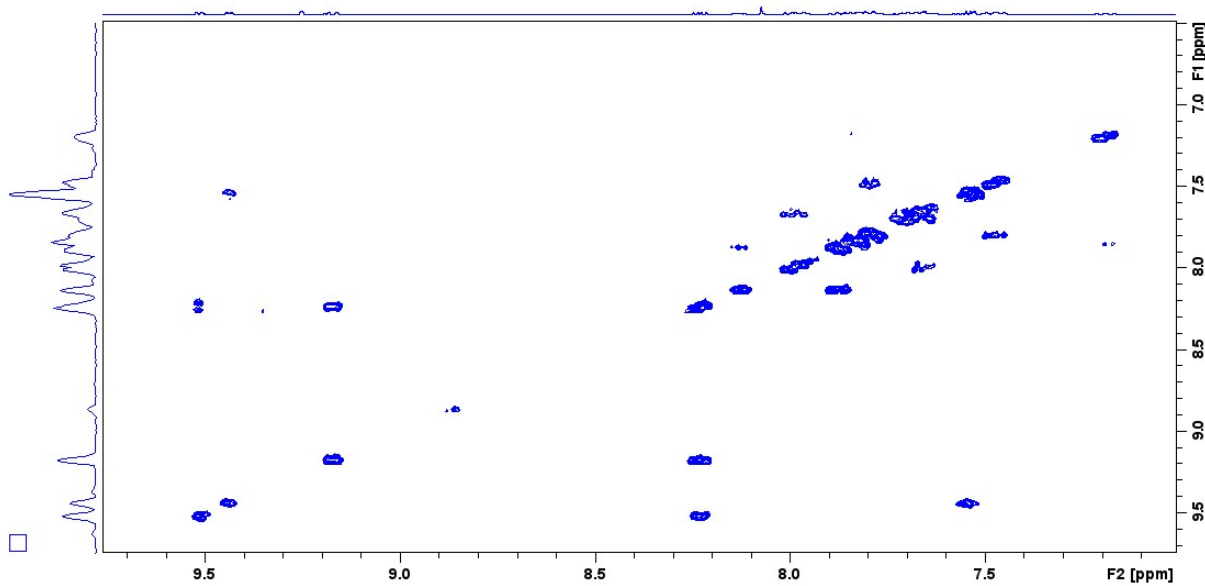


Figure S37. ^1H - ^1H COSY NMR spectrum of **2ReL1** recorded at 400 MHz in d_6 -acetone.

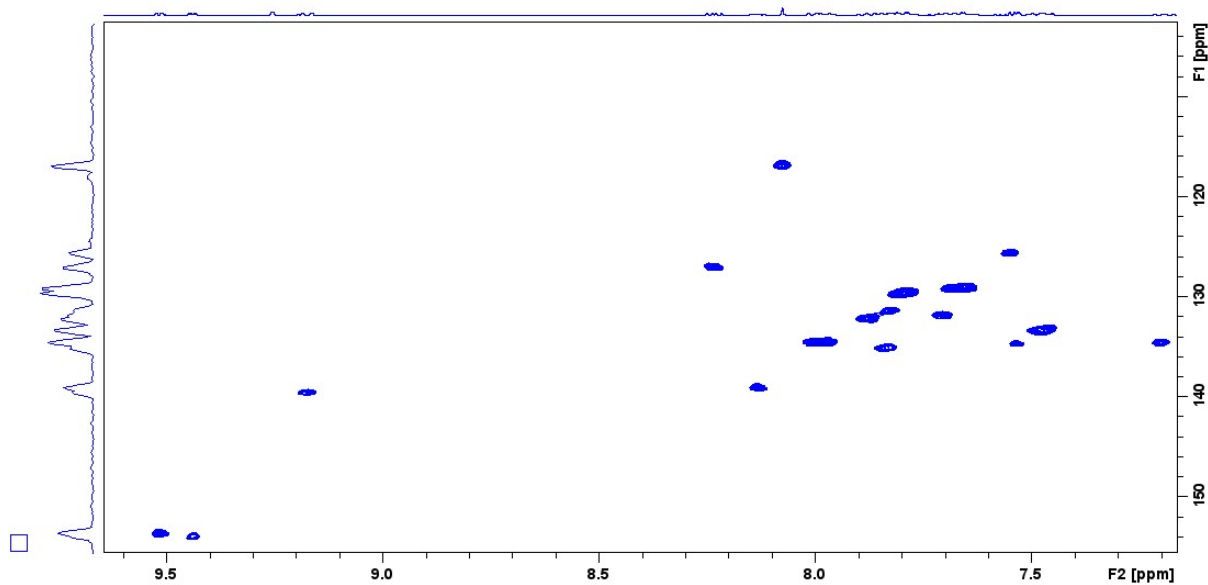
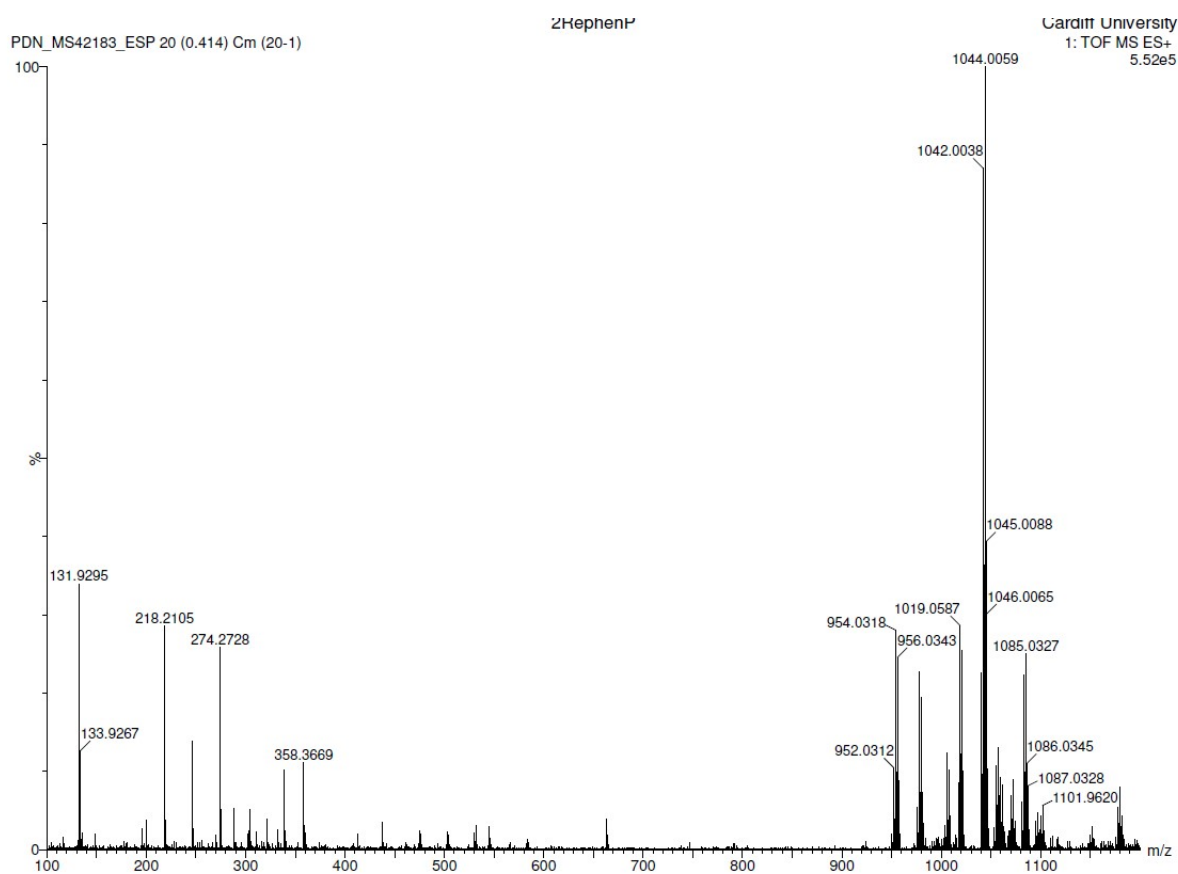


Figure S38. ^1H - ^{13}C HSQC NMR spectrum of **2ReL1** recorded in d_6 -acetone.



Minimum:				-1.5				
Maximum:		5000.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1042.0038	1042.0022	1.6	1.5	28.5	649.6	n/a	n/a	$\text{C}_{37}\text{H}_{22}\text{N}_3\text{O}_6\text{P}\text{Cl}$ 185Re 187Re

Figure S39. HRMS (ES^+) spectrum of **2ReL1**.

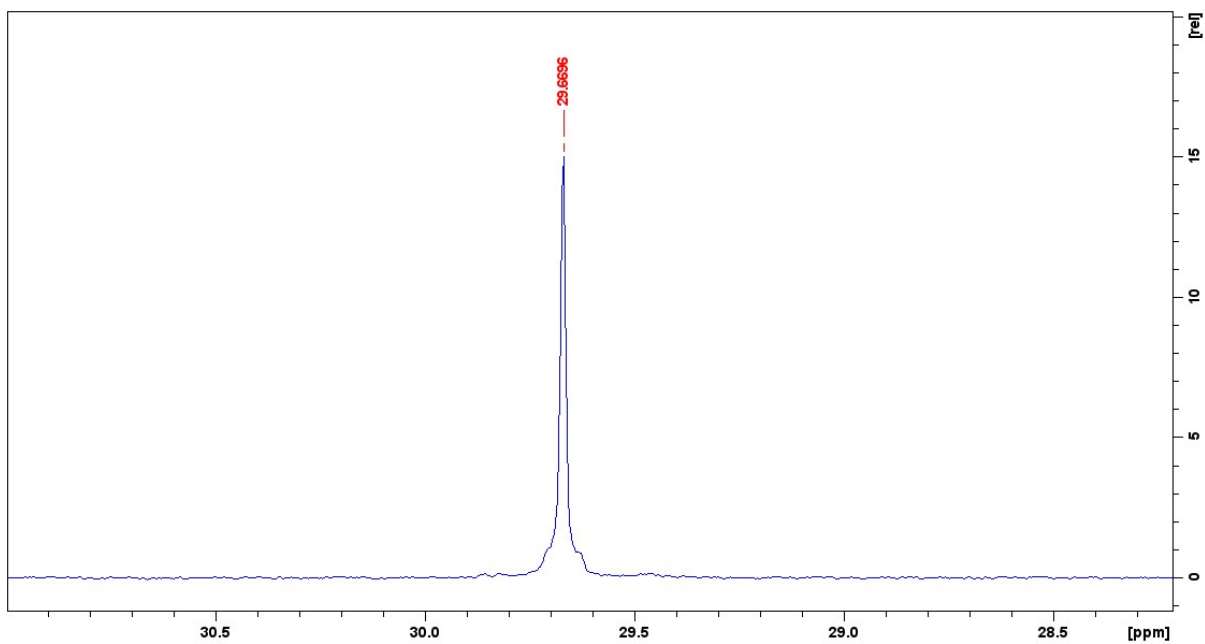


Figure S40. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **ReAuL1** recorded at 162 MHz in CD_2Cl_2 .

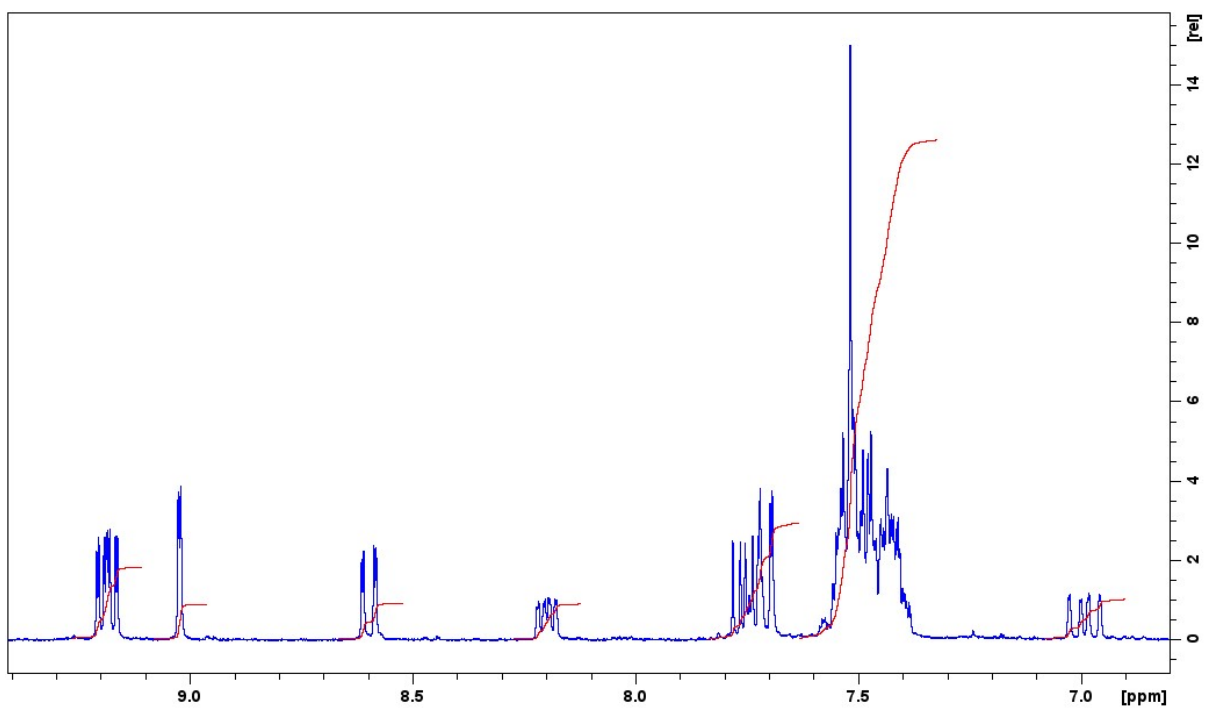


Figure S41 ^1H NMR spectra of **ReAuL1** recorded at 400 MHz in CD_2Cl_2 .

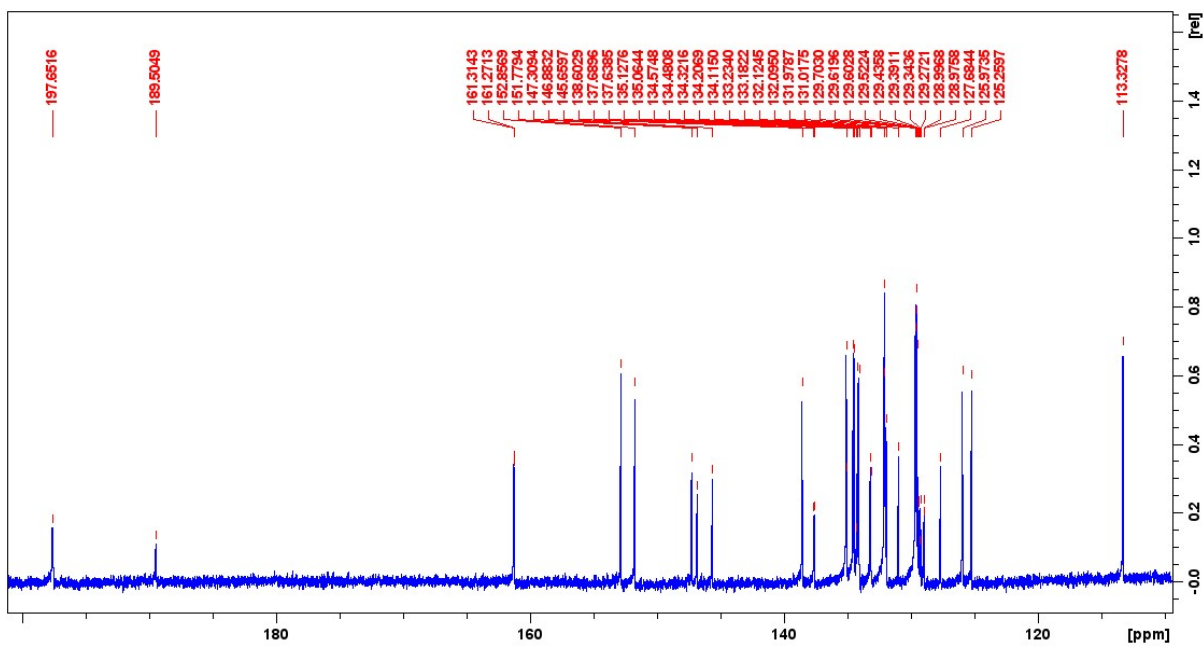


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **ReAuL1** recorded at 75 MHz in CD_2Cl_2 .

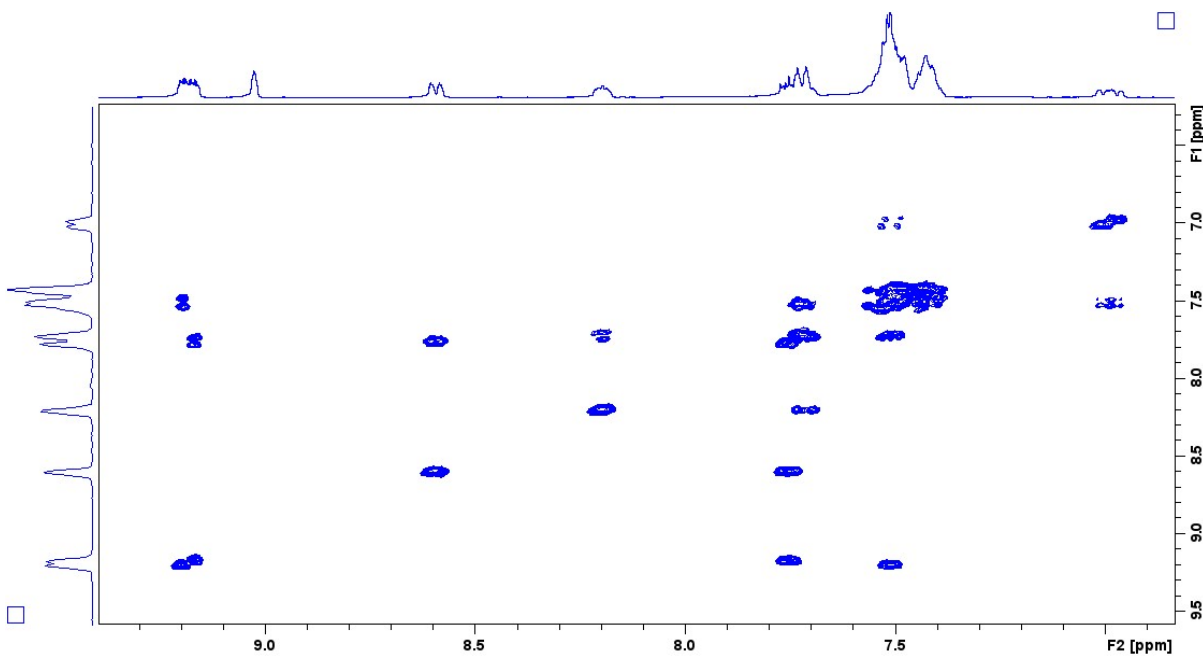


Figure S43. ^1H - ^1H COSY NMR spectrum of **ReAuL1** recorded at 400 MHz in CD_2Cl_2 .

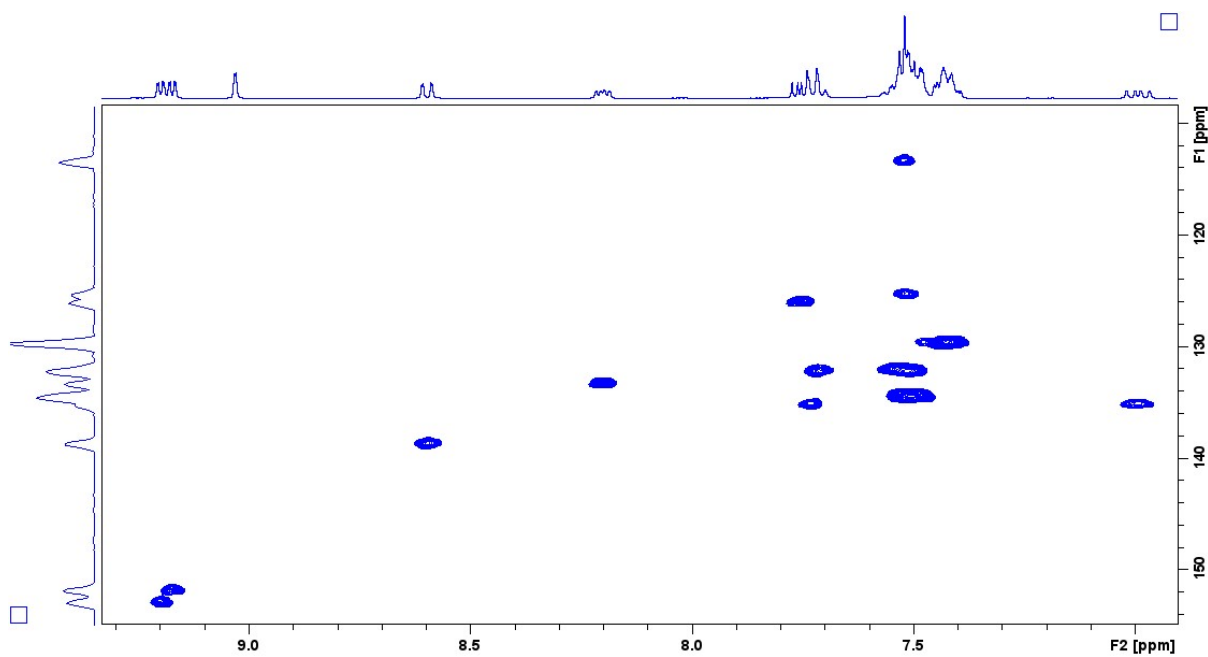


Figure S44. ^1H - ^{13}C HSQC NMR spectrum of **ReAuL1** recorded in CD_2Cl_2 .

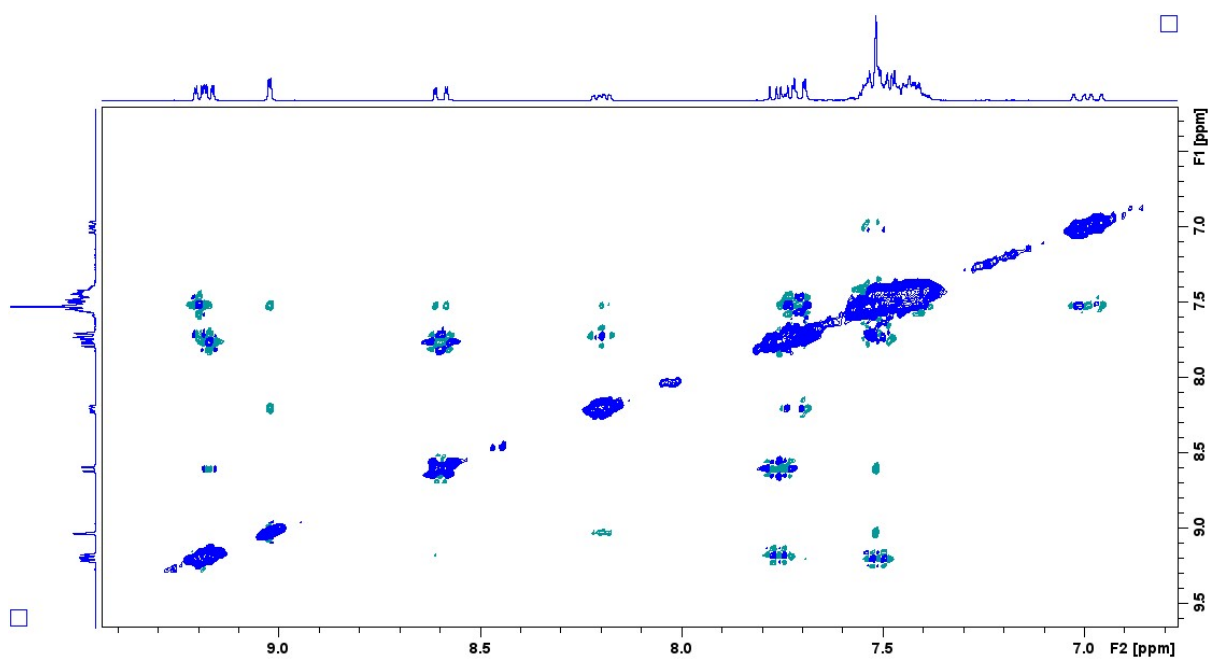
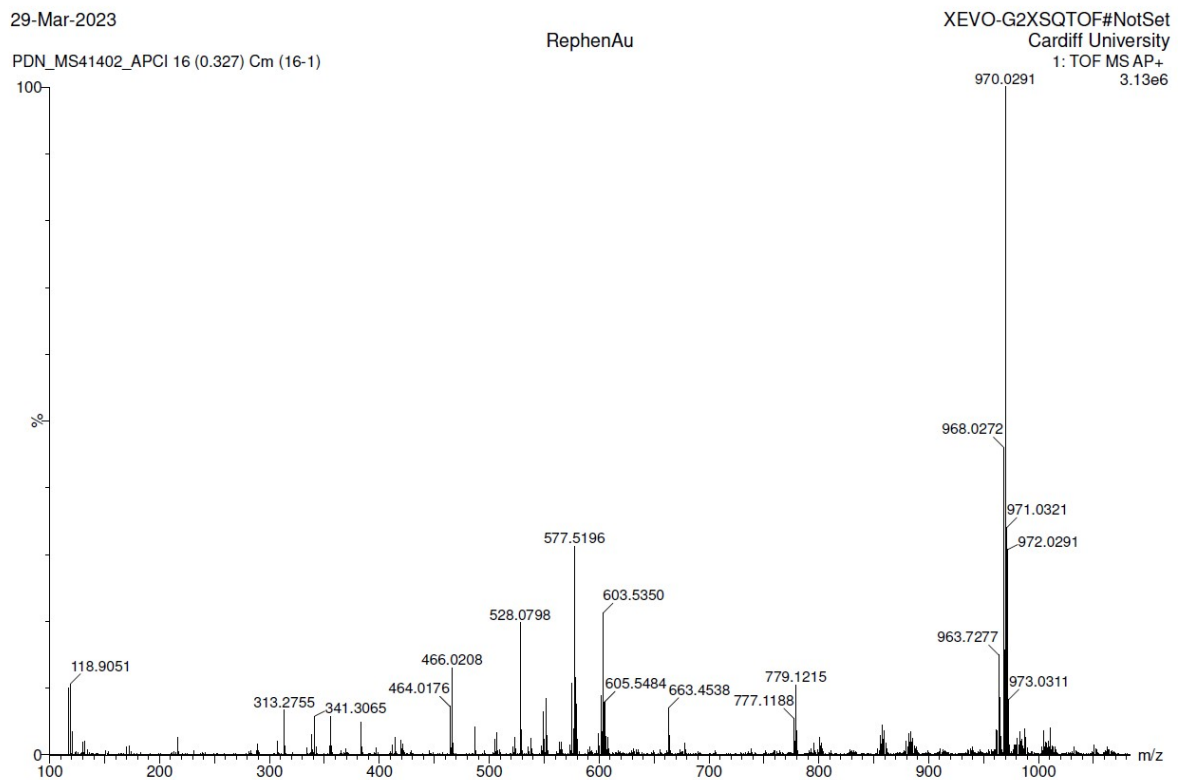


Figure S45. ^1H - ^1H NOESY NMR spectrum of **ReAuL1** recorded at 400 MHz in CD_2Cl_2 .



Minimum:									
Maximum:	5.0	10.0	-1.5	100.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula	
970.0291	970.0310	-1.9	-2.0	26.0	851.0	n/a	n/a	C34 H22 N3 O3 P Cl 187Re 197Au	

Figure S46. HRMS (ES⁺) spectrum of **ReAu1**.

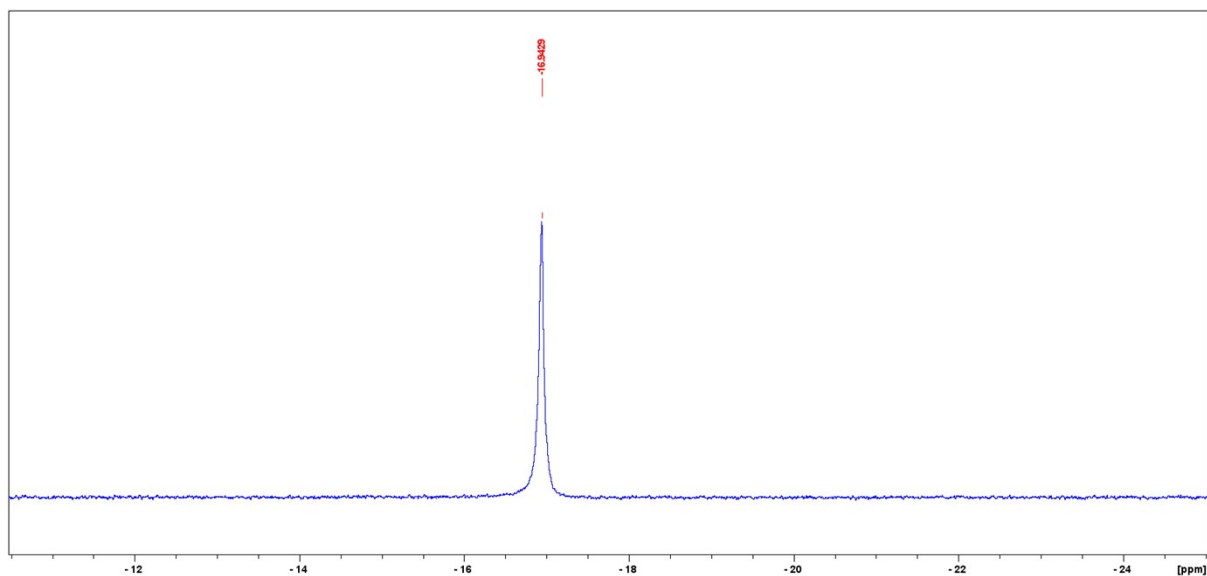


Figure S47. ³¹P{¹H} NMR spectrum of **ReL2** recorded at 162 MHz in d₆-dms_o.

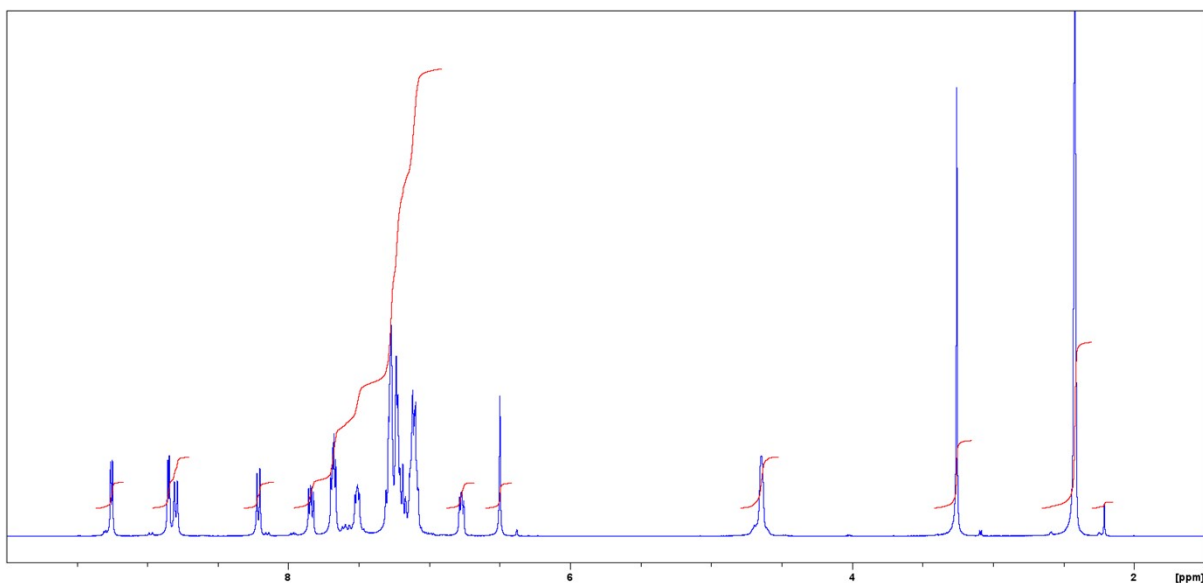


Figure S48. ^1H NMR spectra of ReL2 recorded at 400 MHz in d_6 -dmsO.

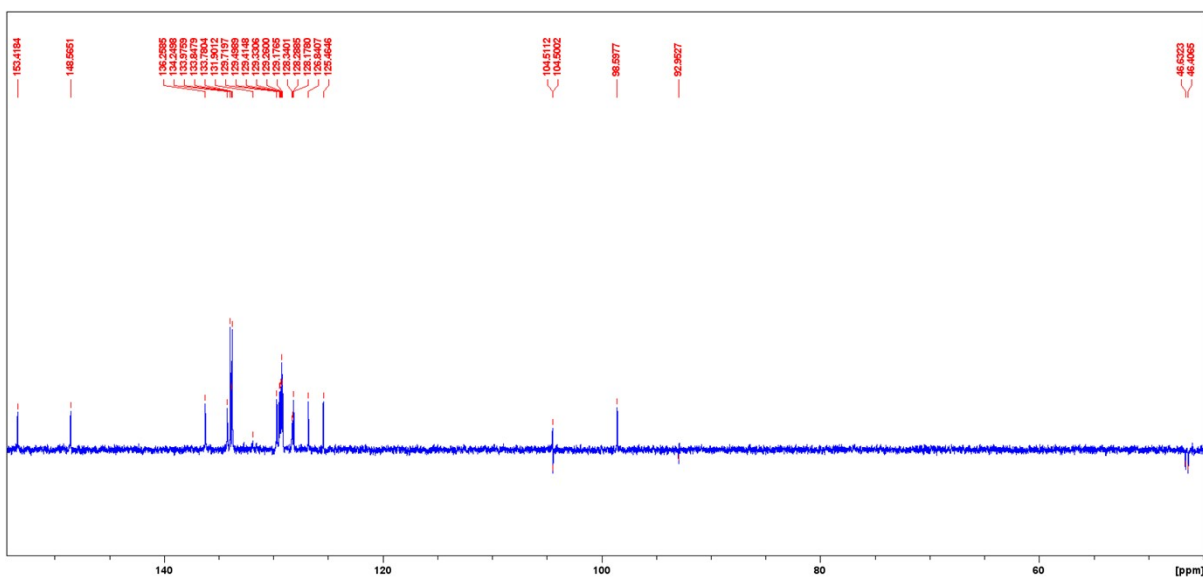
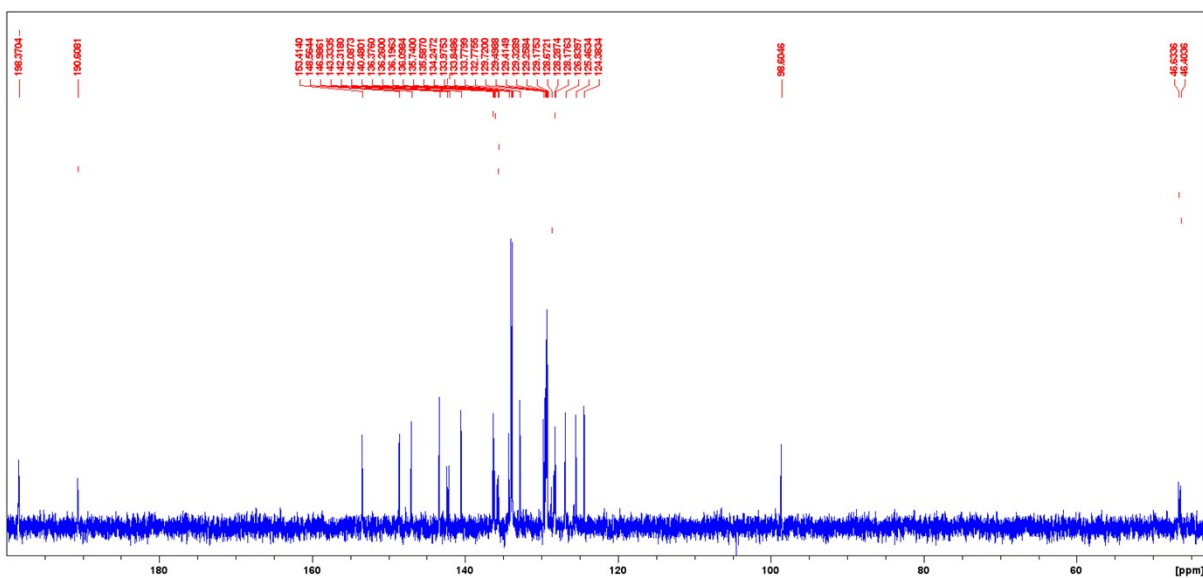


Figure S49. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of ReL2 recorded at 75 MHz in d_6 -dmsO.

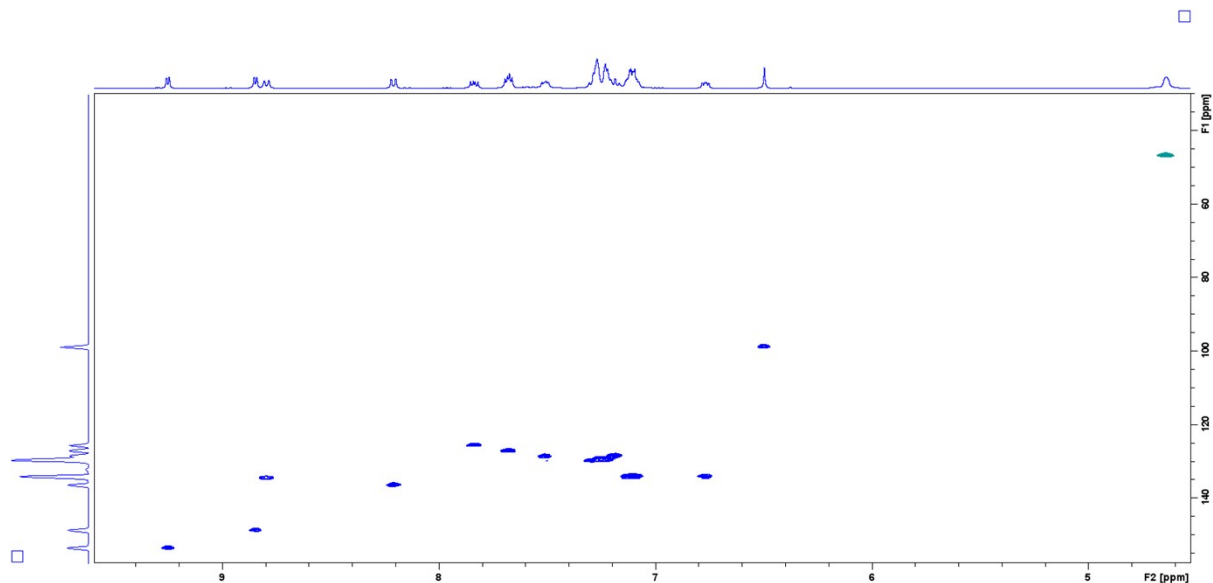


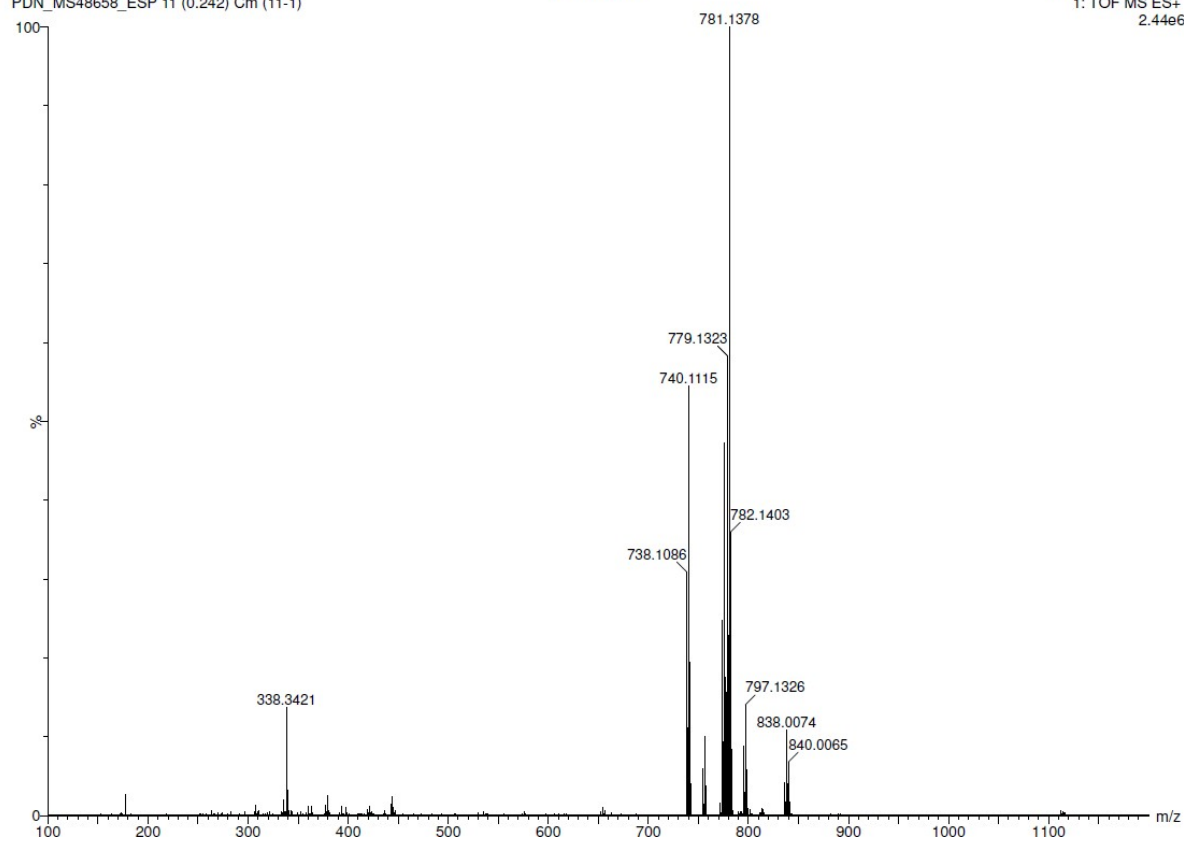
Figure S50. ^1H - ^{13}C HSQC NMR spectrum of **ReL2** recorded in d_6 - dmsO .

25-Oct-2023

PDN_MS48658_ESP 11 (0.242) Cm (11-1)

RephenPR

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
2.44e6



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
740.1115	740.1113	0.2	0.3	25.0	949.0	n/a	n/a	C34 H24 N3 O3 P 187Re

Figure S51. HRMS (ES^+) spectrum of **ReL2**.

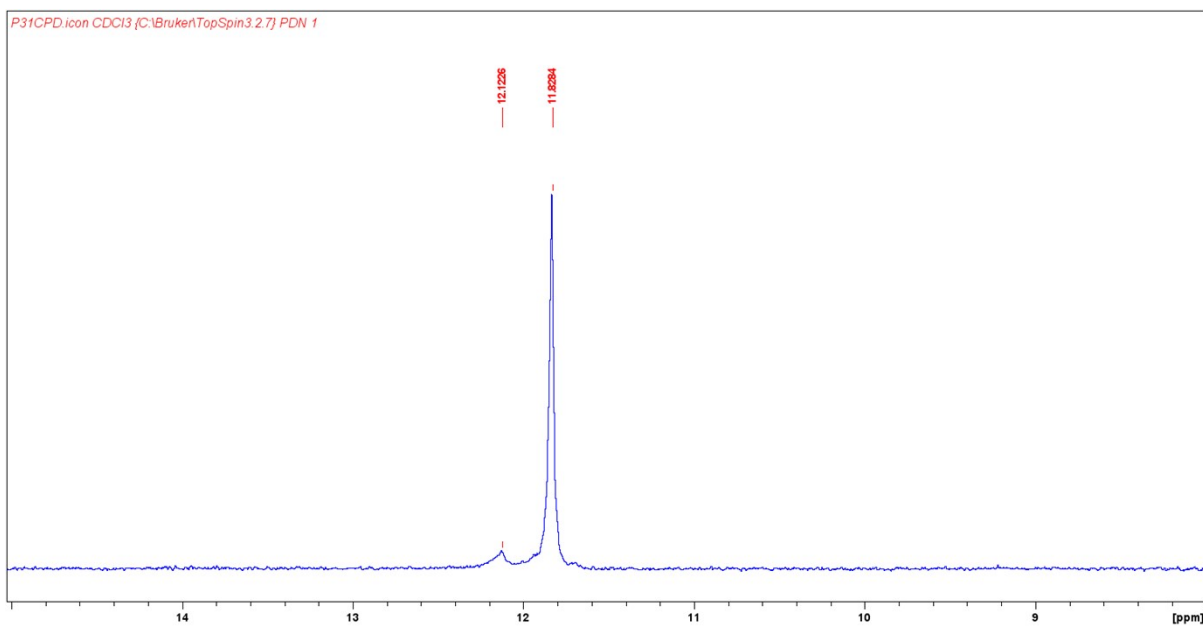


Figure S52. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2ReL2** recorded at 162 MHz in CDCl_3 .

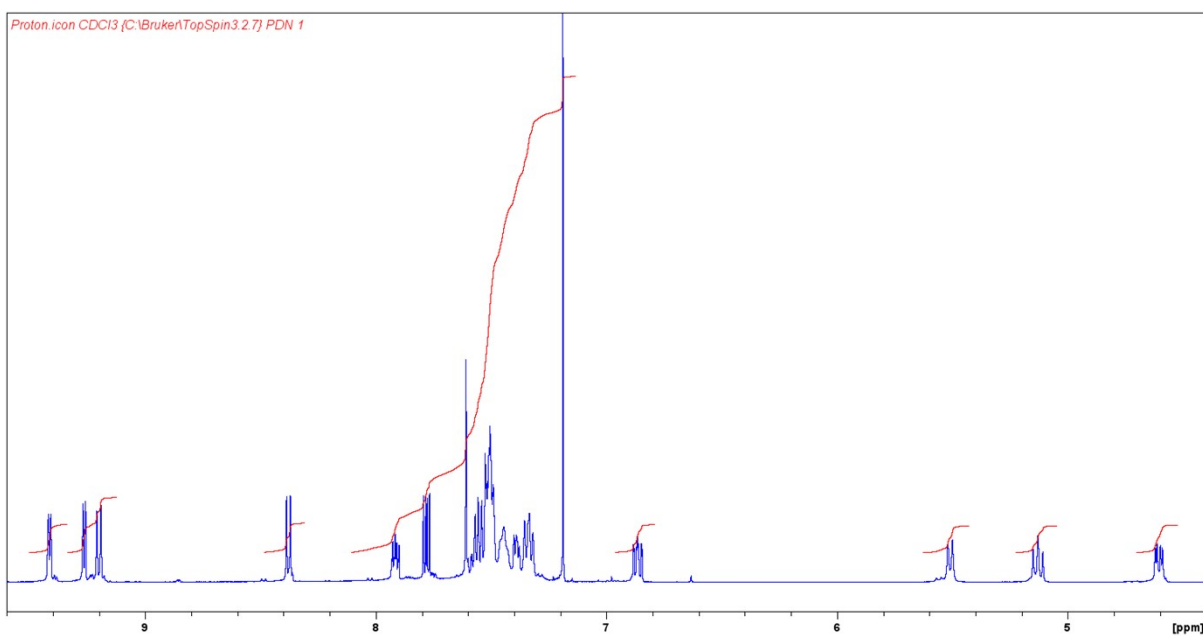


Figure S53. ^1H NMR spectra of **2ReL2** recorded at 400 MHz in CDCl_3 .

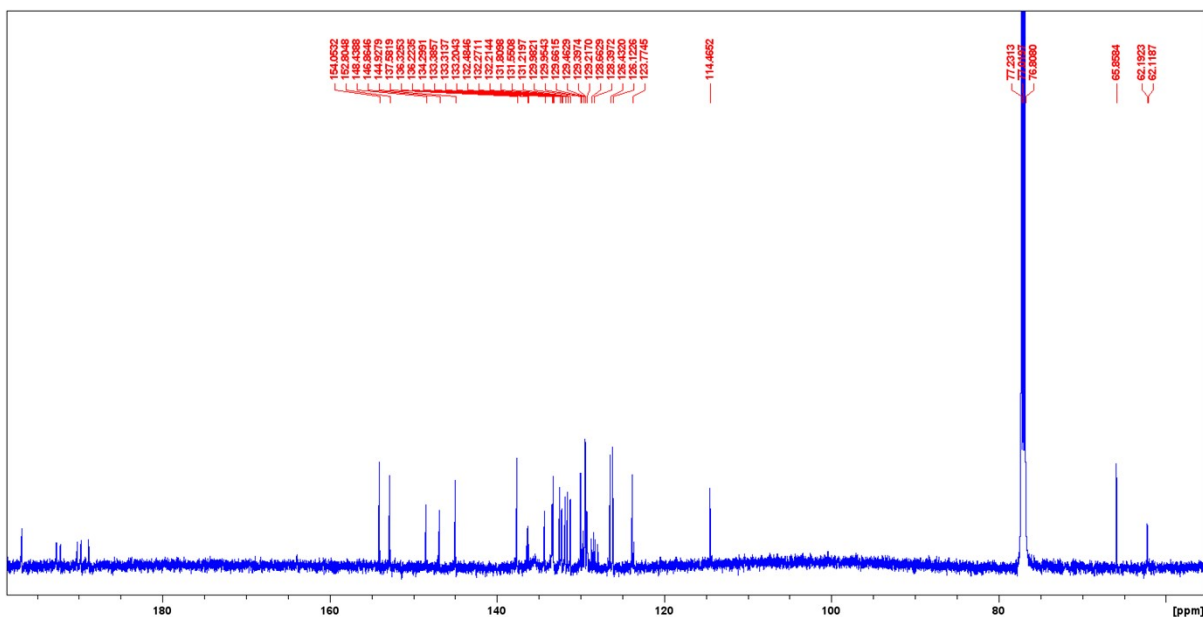


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2ReL2** recorded at 75 MHz in CDCl_3 .

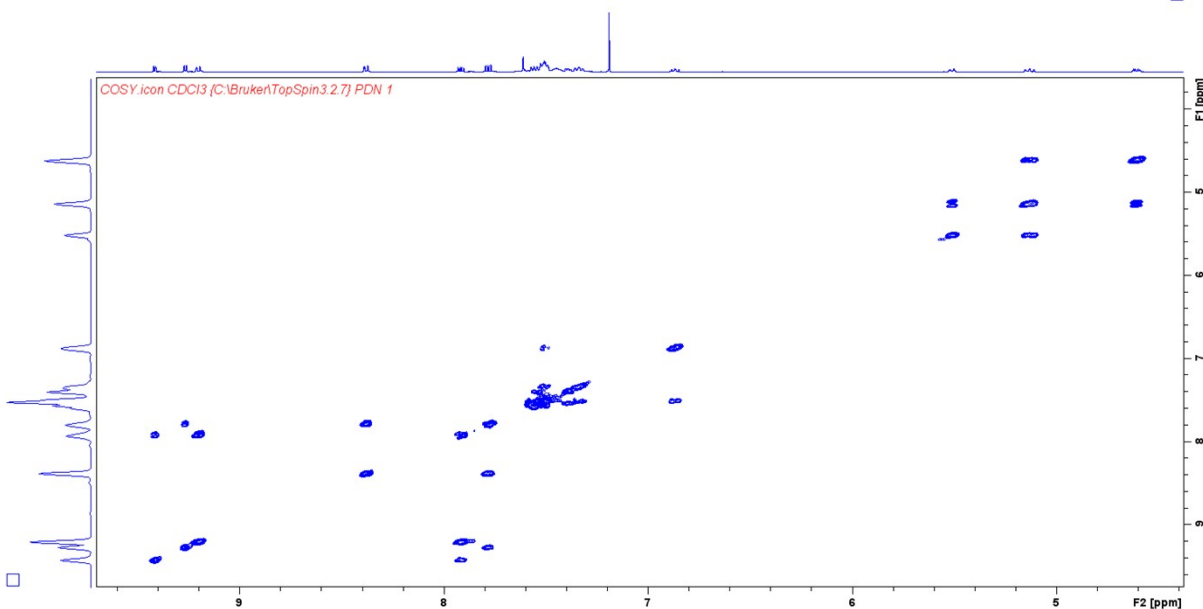


Figure S55. ^1H - ^1H COSY NMR spectrum of **2ReL2** recorded at 400 MHz in CDCl_3 .

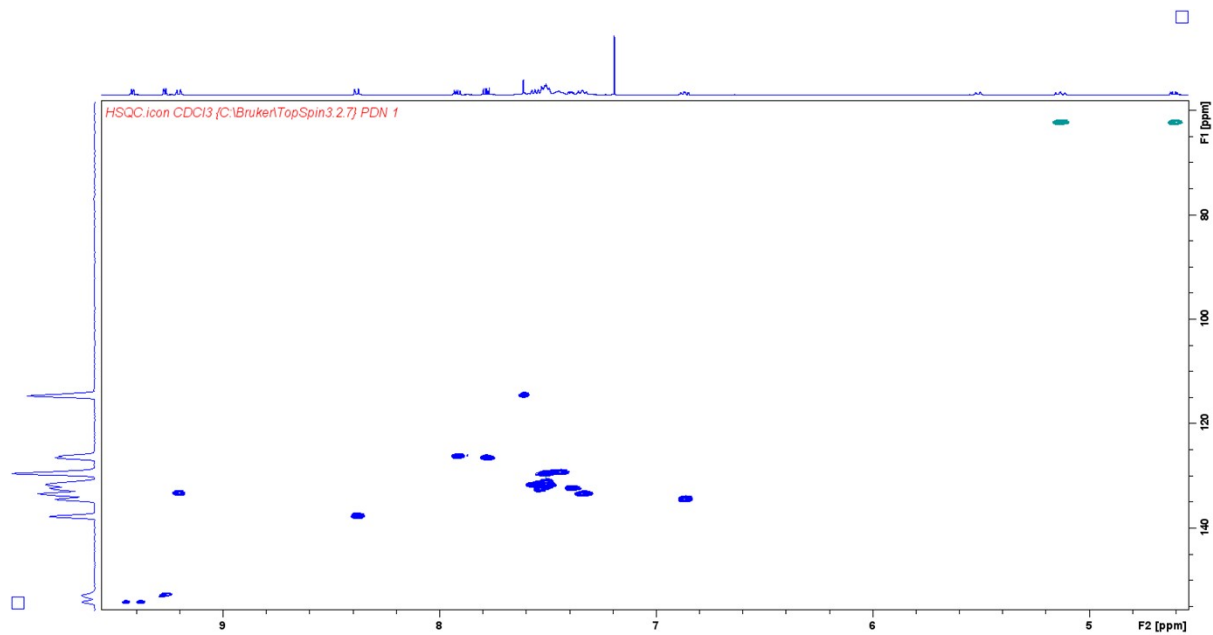


Figure S56. ¹H-¹³C HSQC NMR spectrum of **2ReL2** recorded in CDCl₃.

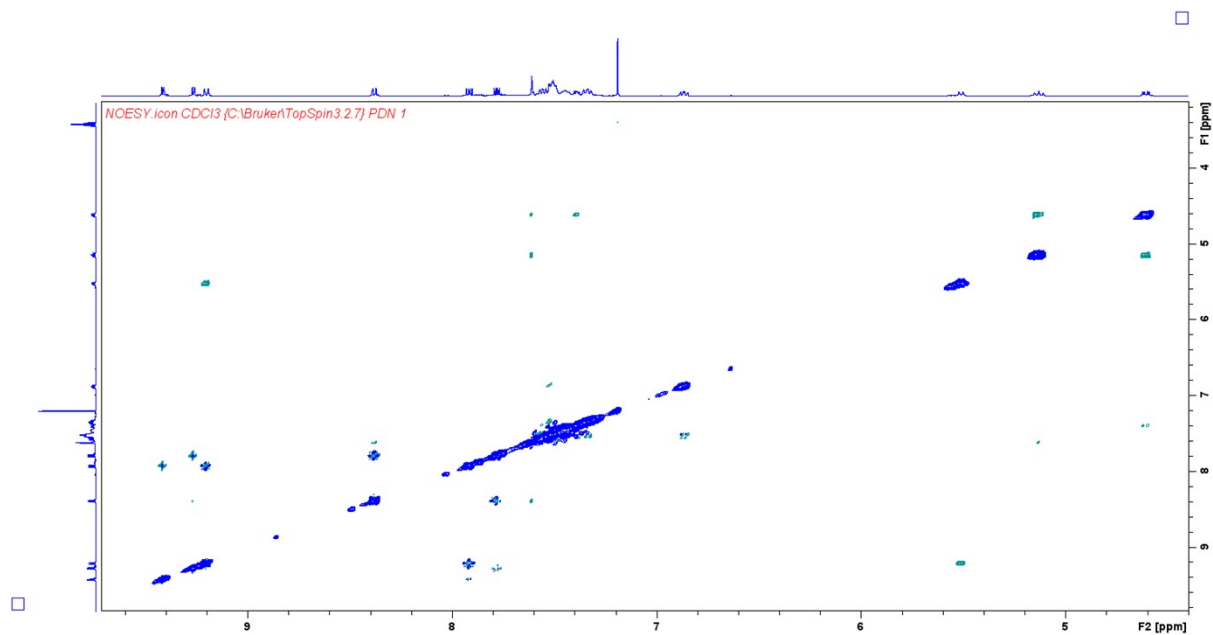


Figure S57. ¹H-¹H NOESY NMR spectrum of **2ReL2** recorded at 400 MHz in CDCl₃.

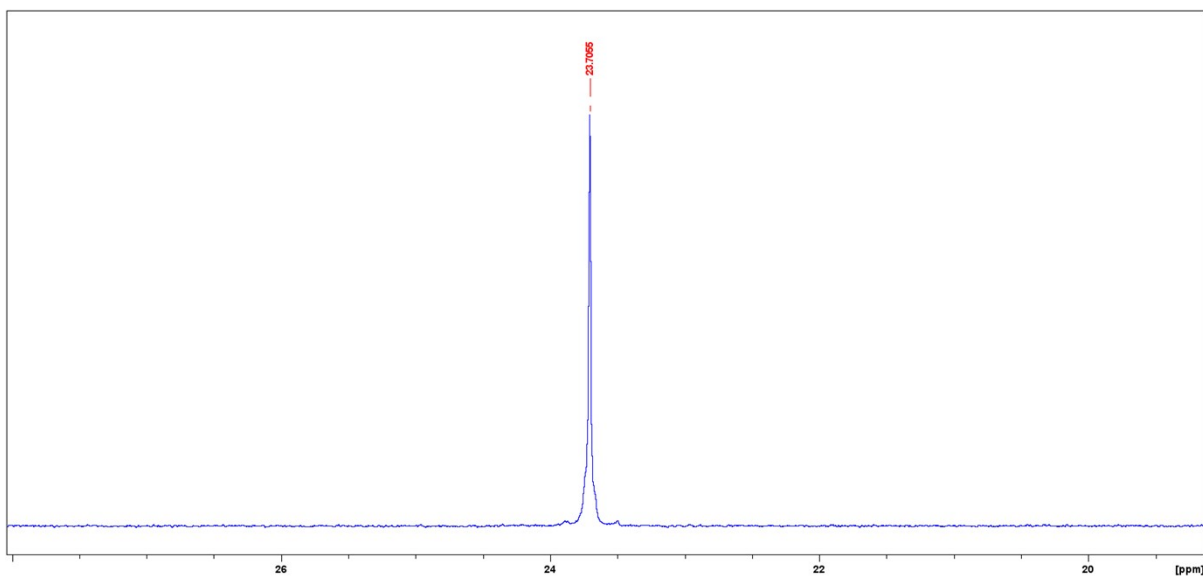


Figure S58. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **ReAuL2** recorded at 162 MHz in CDCl_3 .

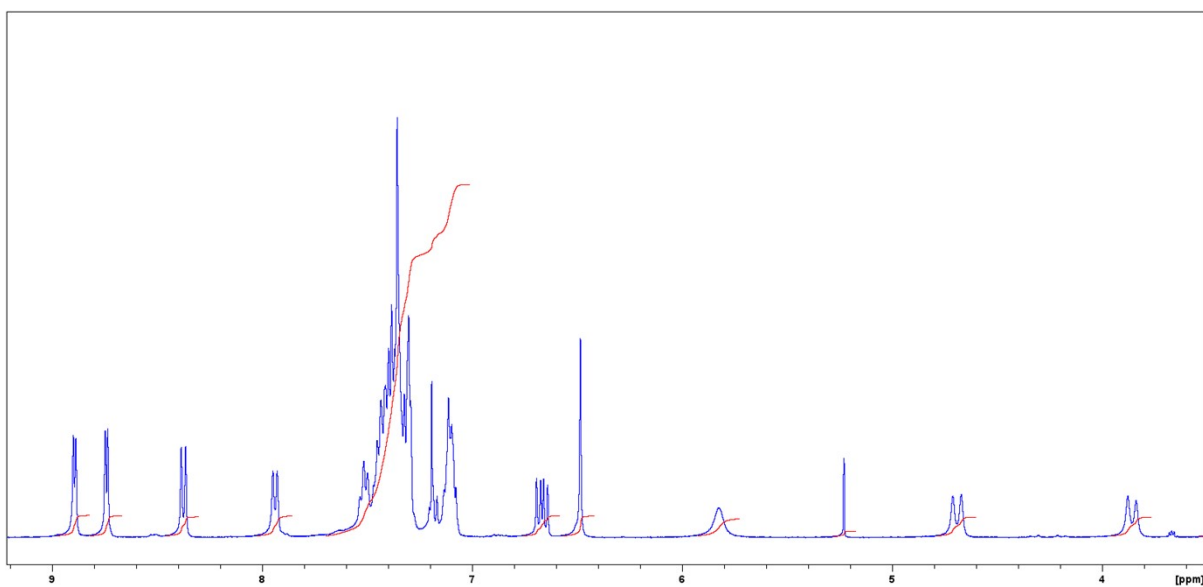


Figure S59. ^1H NMR spectra of **ReAuL2** recorded at 400 MHz in CDCl_3 .

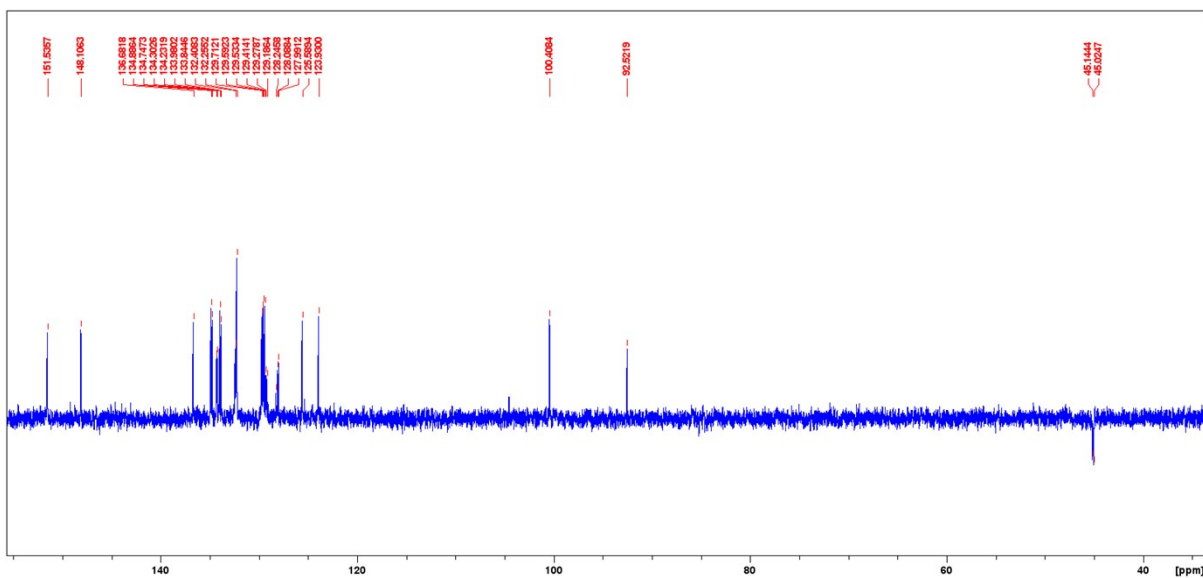
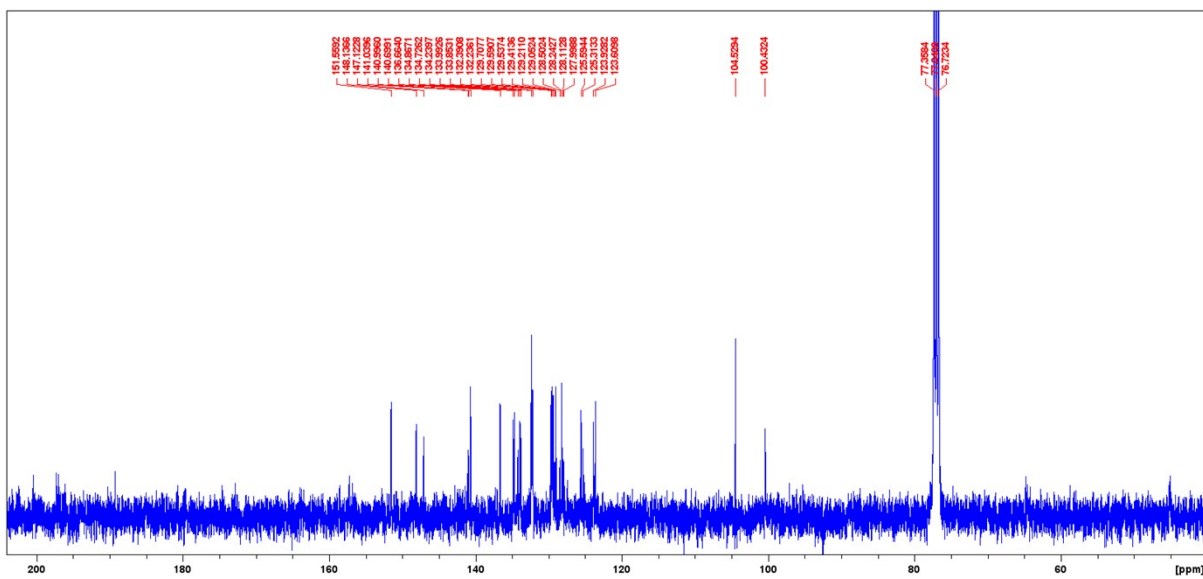


Figure S60. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **ReAuL2** recorded at 75 MHz in CDCl_3 .

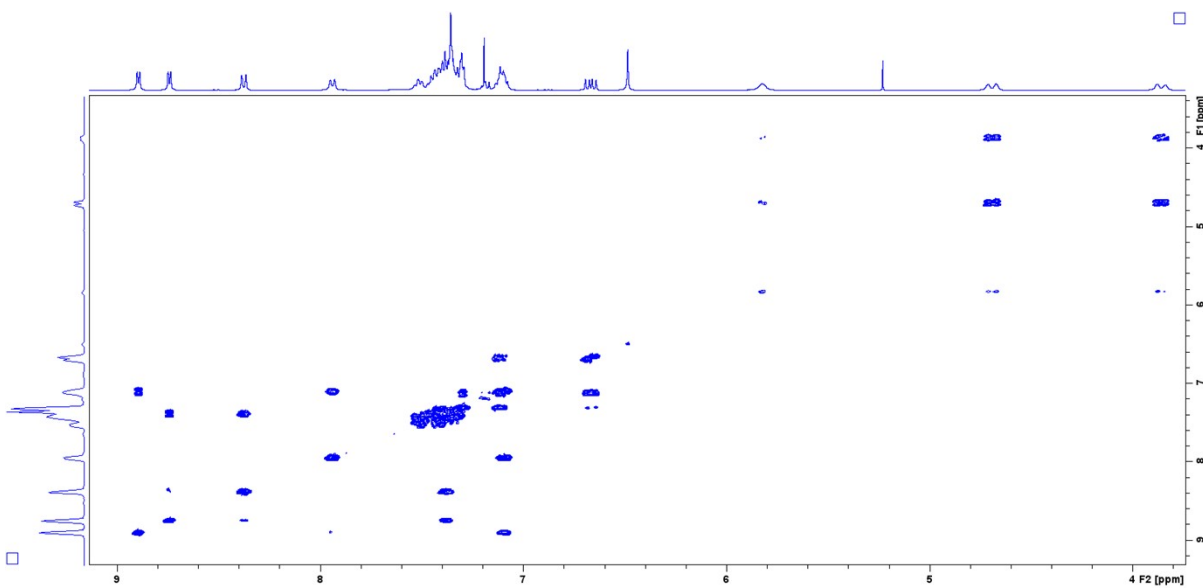


Figure S61. ^1H - ^1H COSY NMR spectrum of **ReAuL2** recorded at 400 MHz in CDCl_3 .

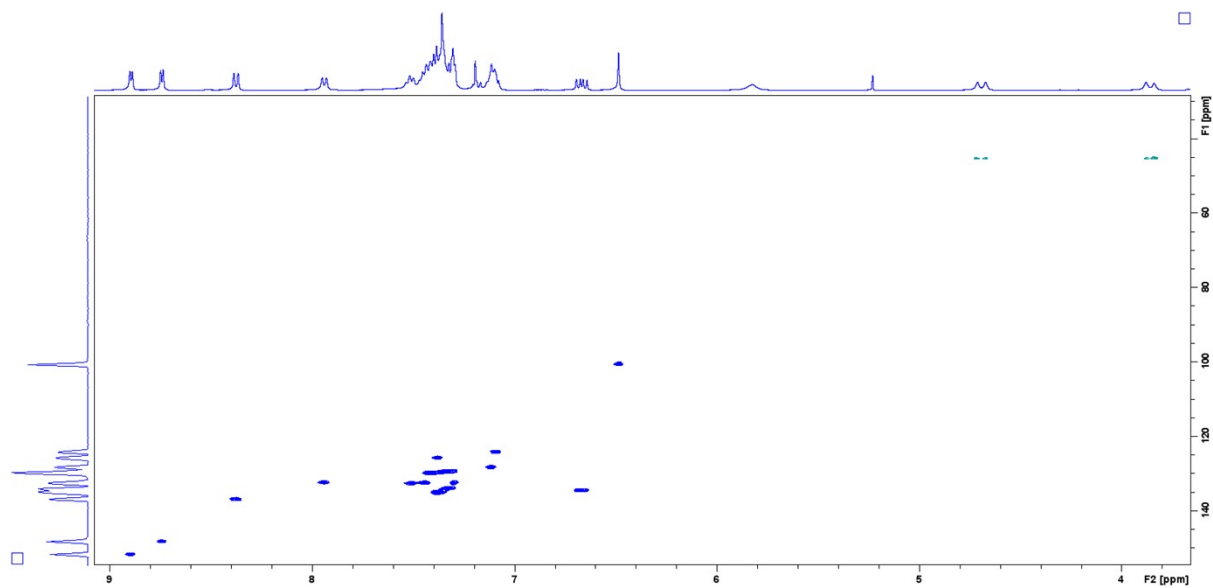


Figure S62. ^1H - ^{13}C HSQC NMR spectrum of **ReAuL2** recorded in CDCl_3 .

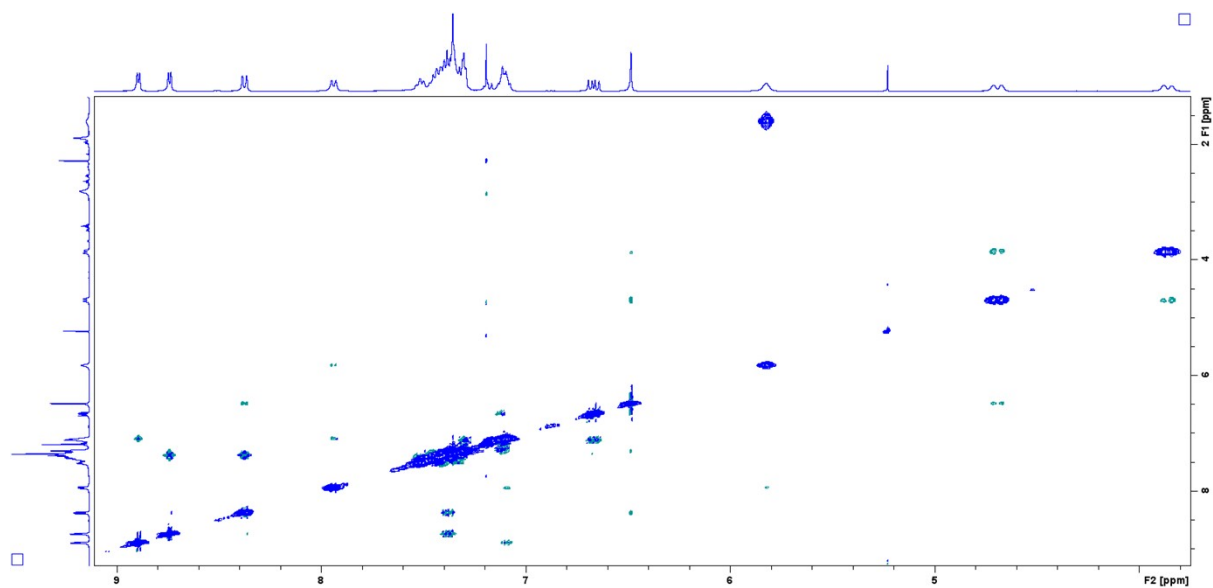


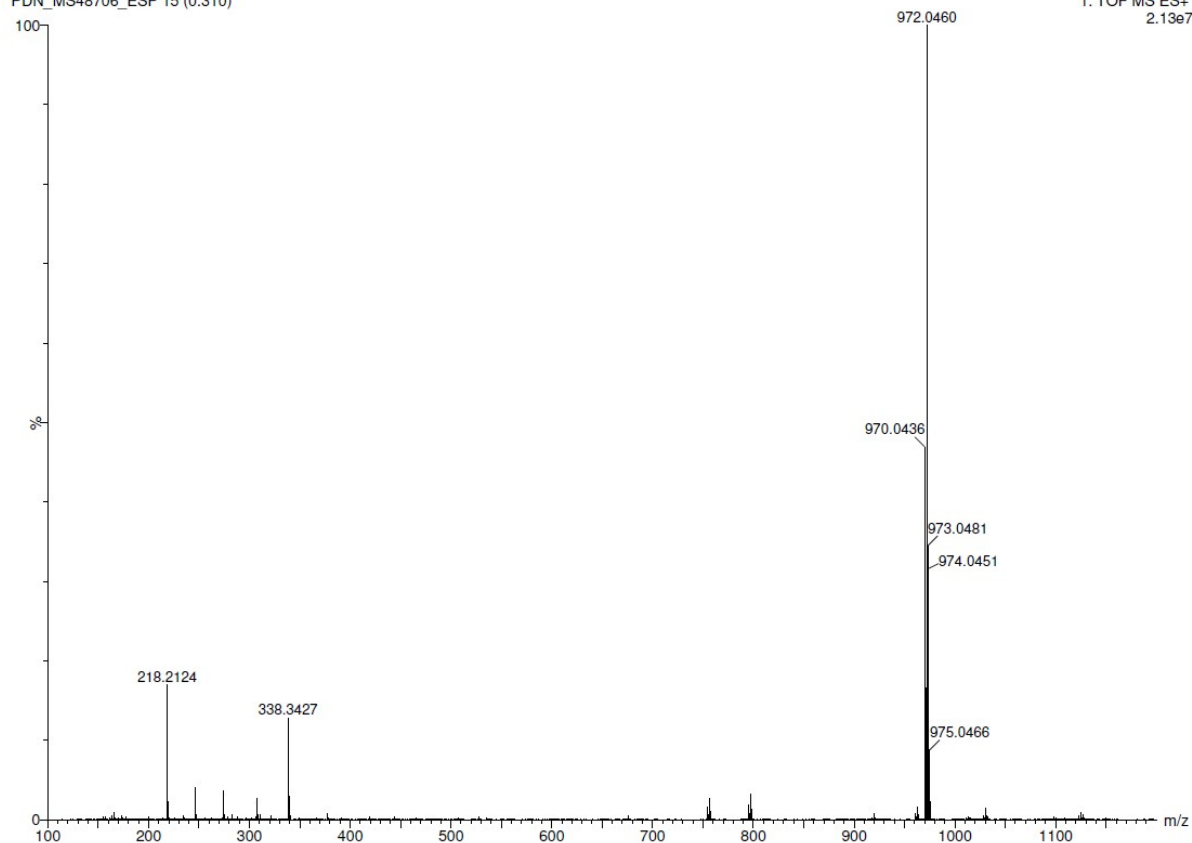
Figure S63. ^1H - ^1H NOESY NMR spectrum of **ReAuL2** recorded at 400 MHz in CDCl_3 .

31-Oct-2023

ReAuL2

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
2.13e7

PDN_MS48706_ESP 15 (0.310)



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
972.0460	972.0467	-0.7	-0.7	25.0	952.5	n/a	n/a	C34 H24 N3 O3 P Cl 187Re 197Au

Figure S64. HRMS (ES⁺) spectrum of ReAuL2.

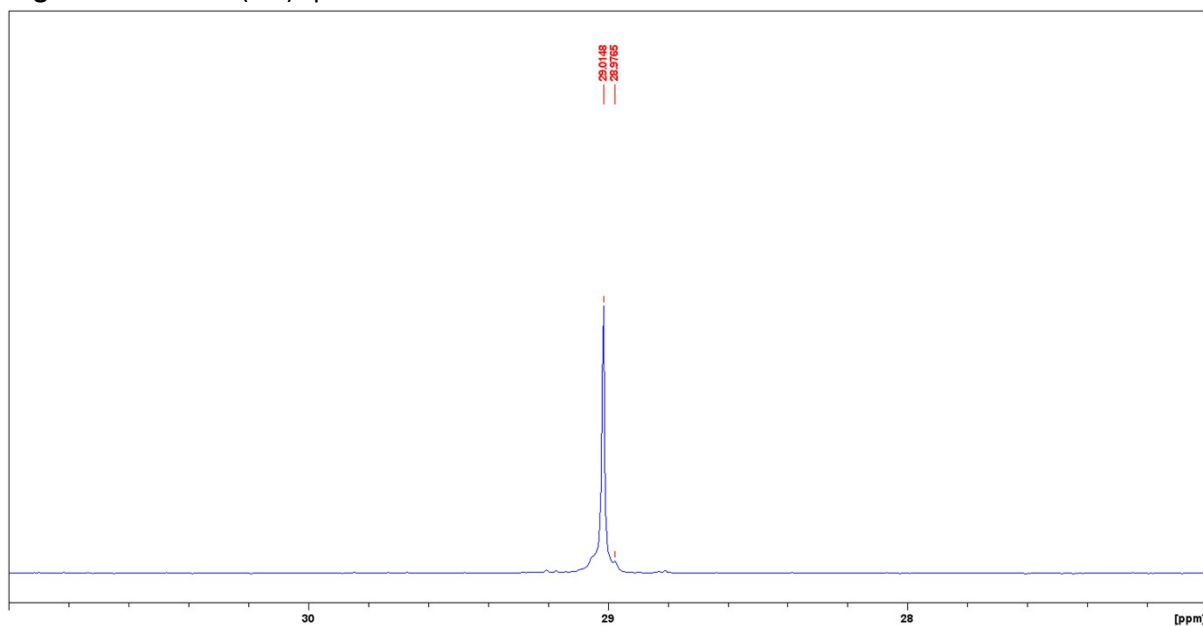


Figure S65. ³¹P{¹H} NMR spectrum of AuL1 recorded at 162 MHz in CDCl₃.

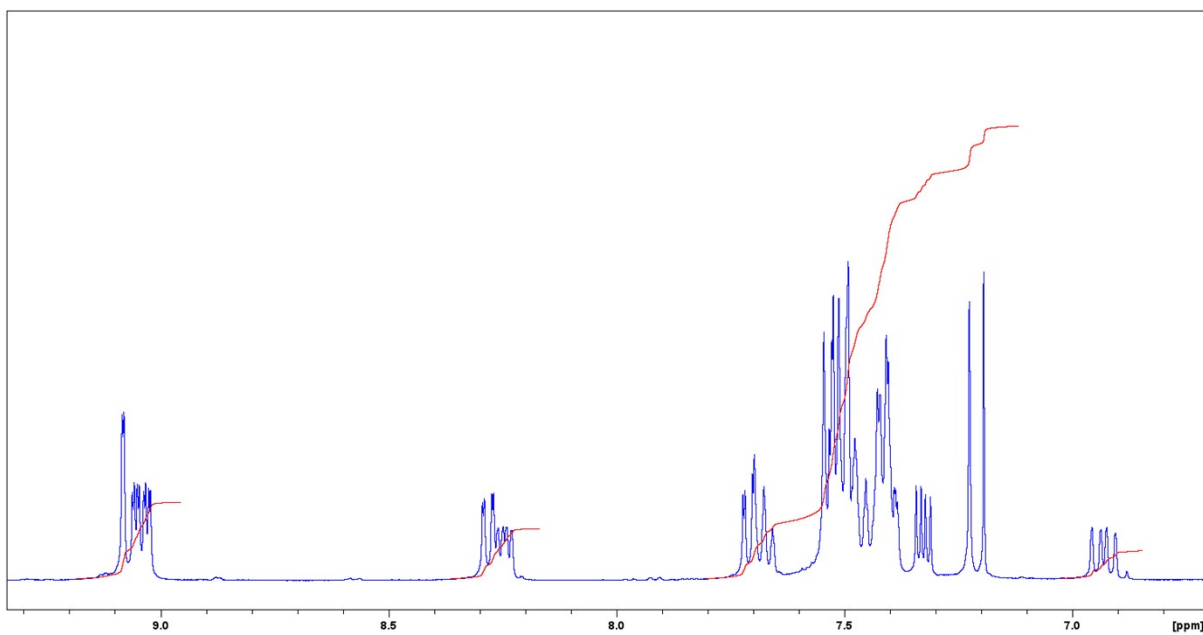
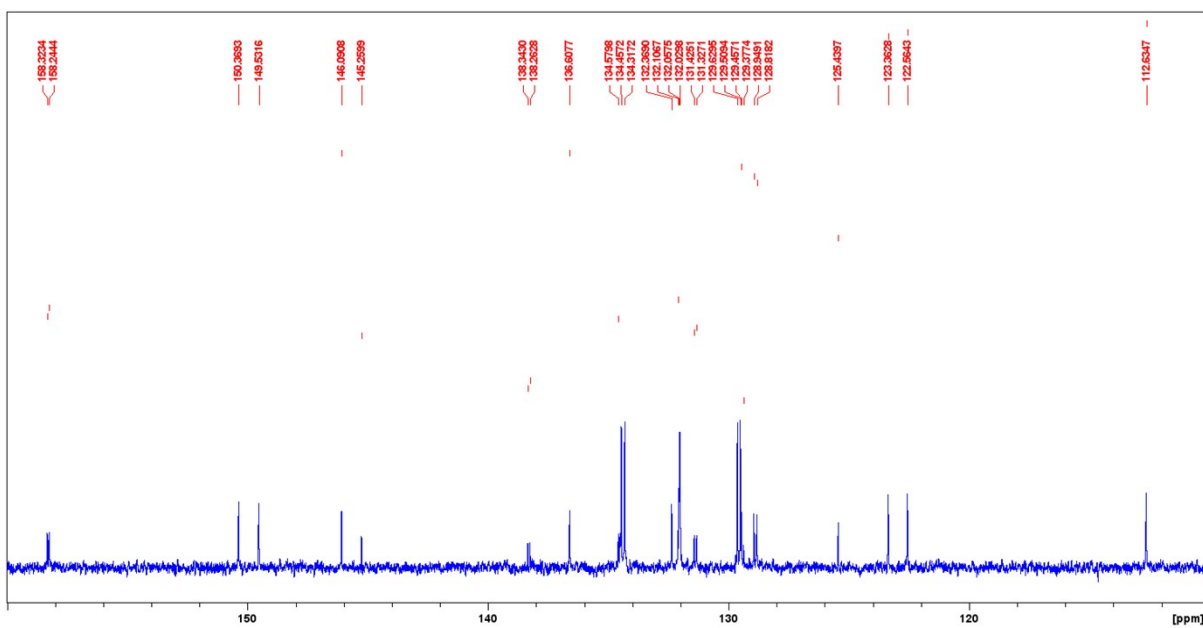


Figure S66. ^1H NMR spectra of **AuL1** recorded at 400 MHz in CDCl_3 .



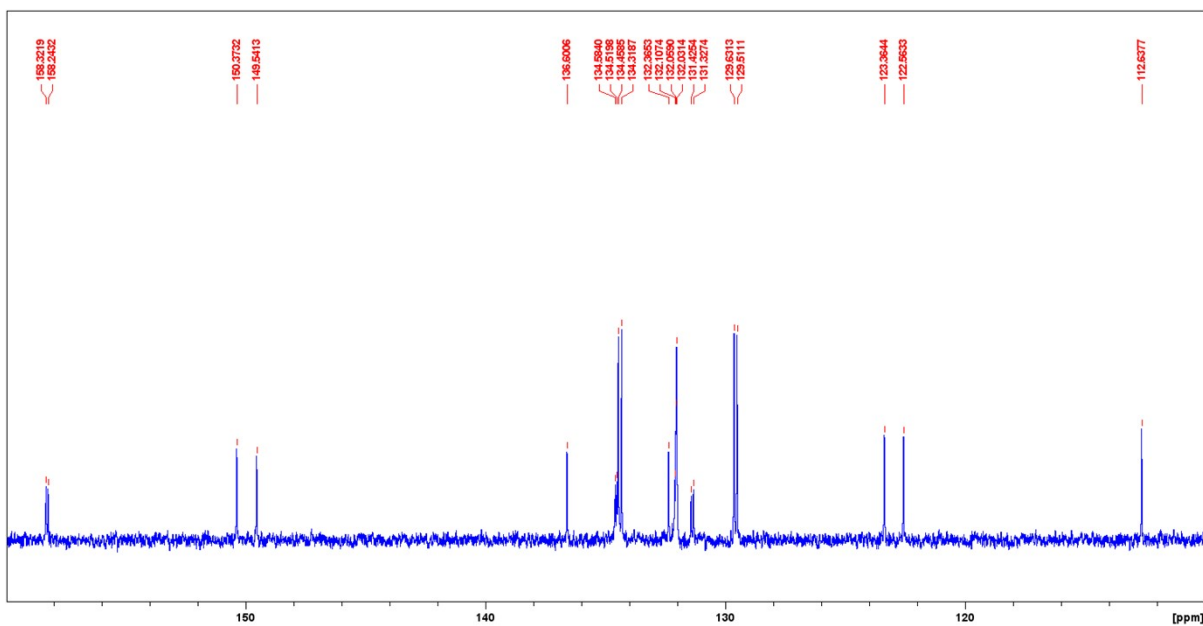


Figure S67. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **AuL1** recorded at 75 MHz in CDCl_3 .

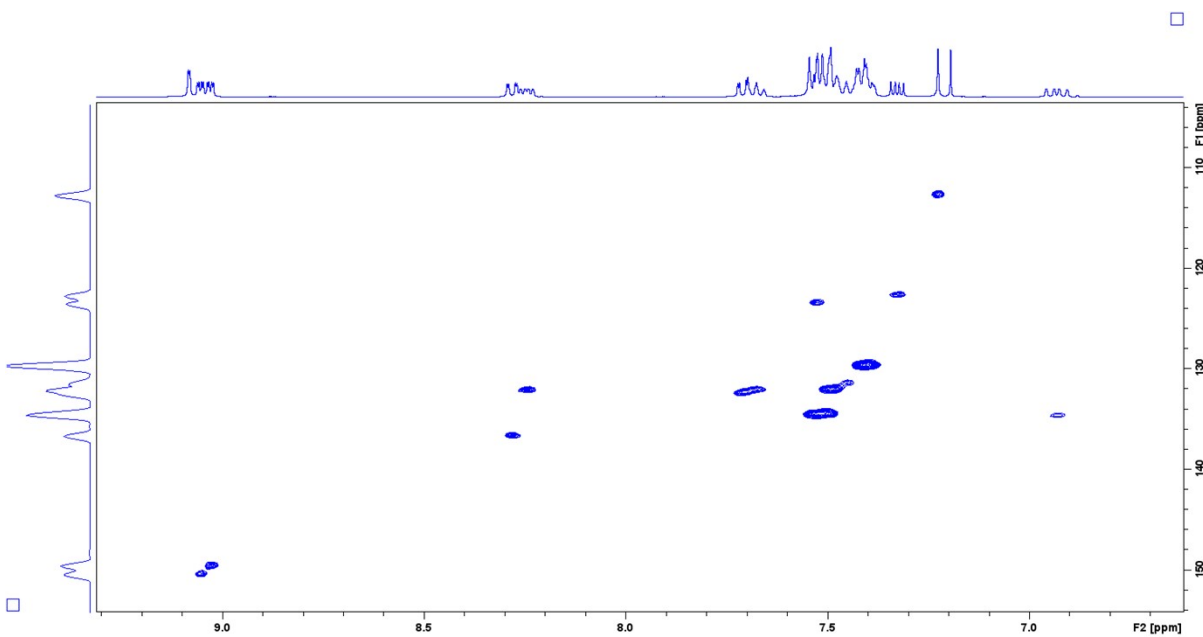


Figure S68. ^1H - ^{13}C HSQC NMR spectrum of **AuL1** recorded in CDCl_3 .

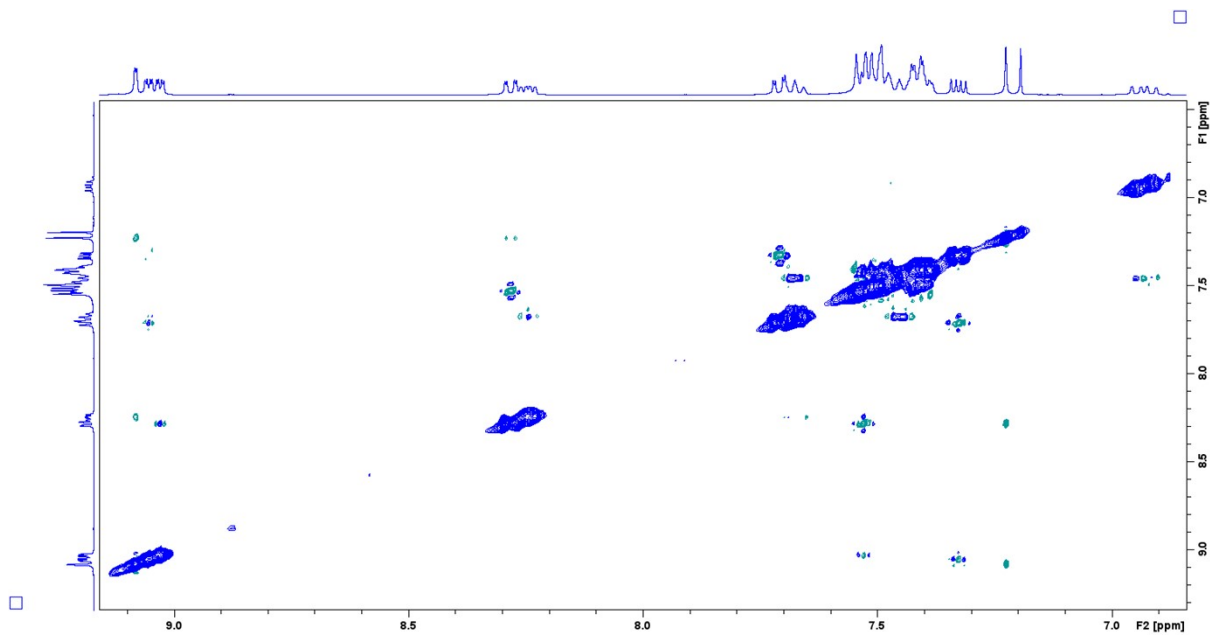
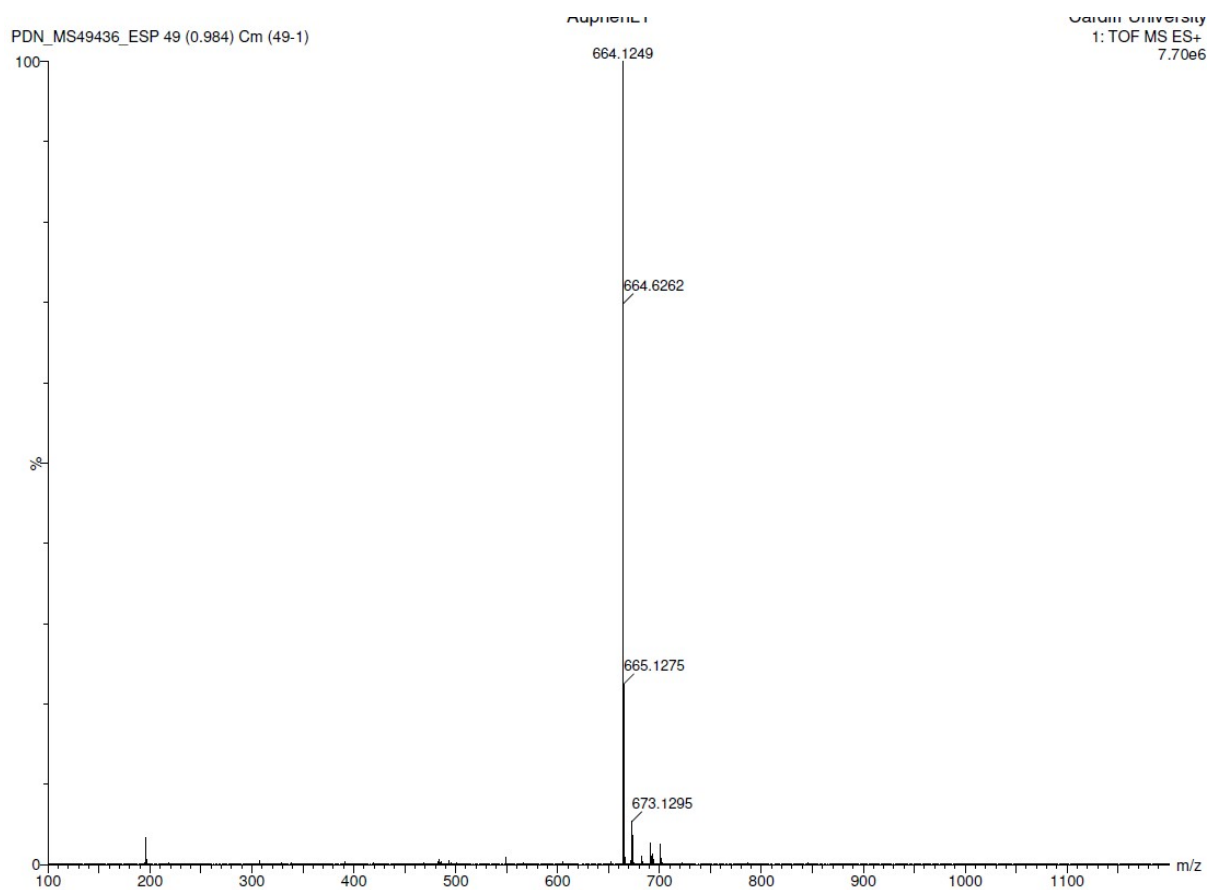


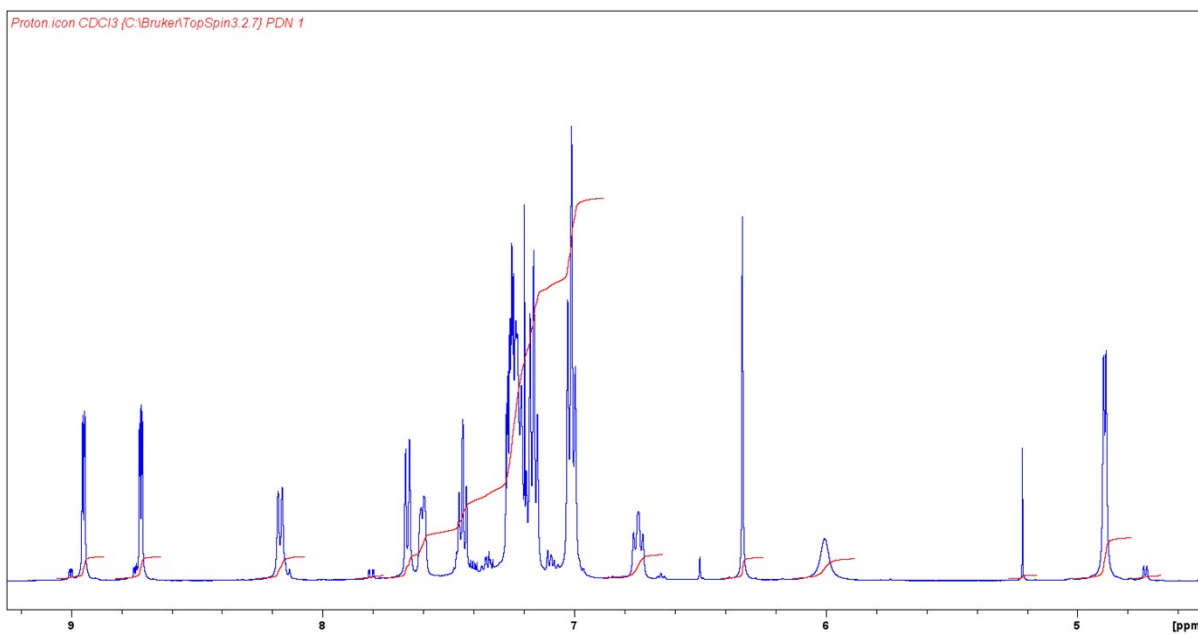
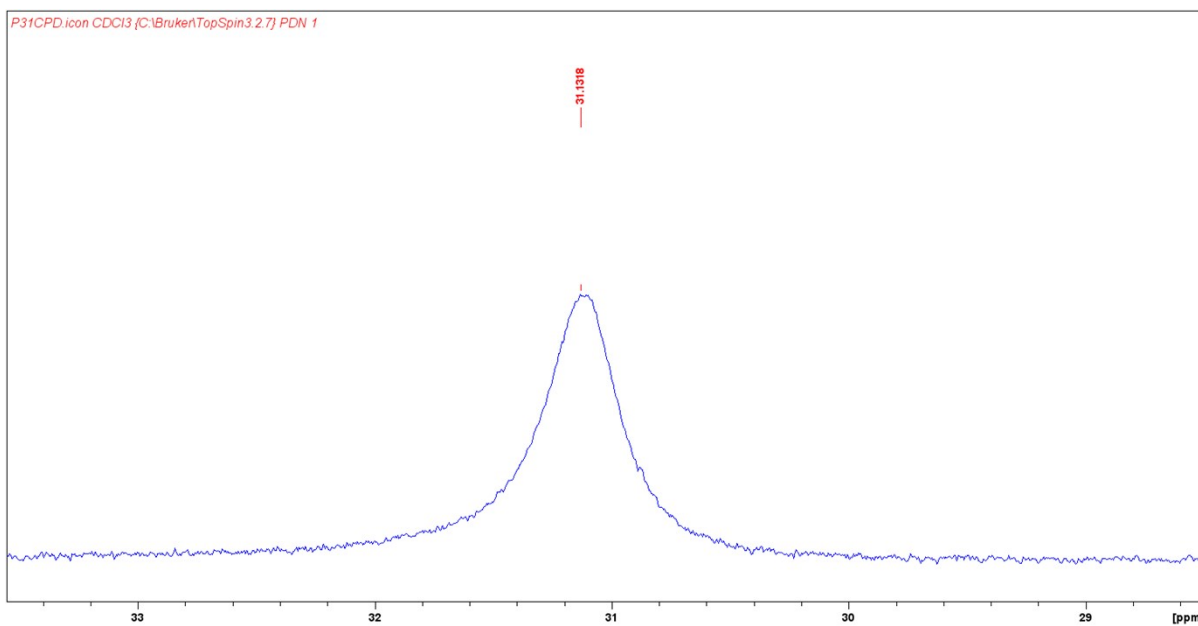
Figure S69. ^1H - ^1H NOESY NMR spectrum of **AuL1** recorded at 400 MHz in CDCl_3 .



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
664.1249	664.1217	3.2	4.8	23.5	1126.4	n/a	n/a	$\text{C}_{31}\text{H}_{22}\text{N}_3\text{P Au}$

Figure S70. HRMS (ES^+) spectrum of **AuL1**.



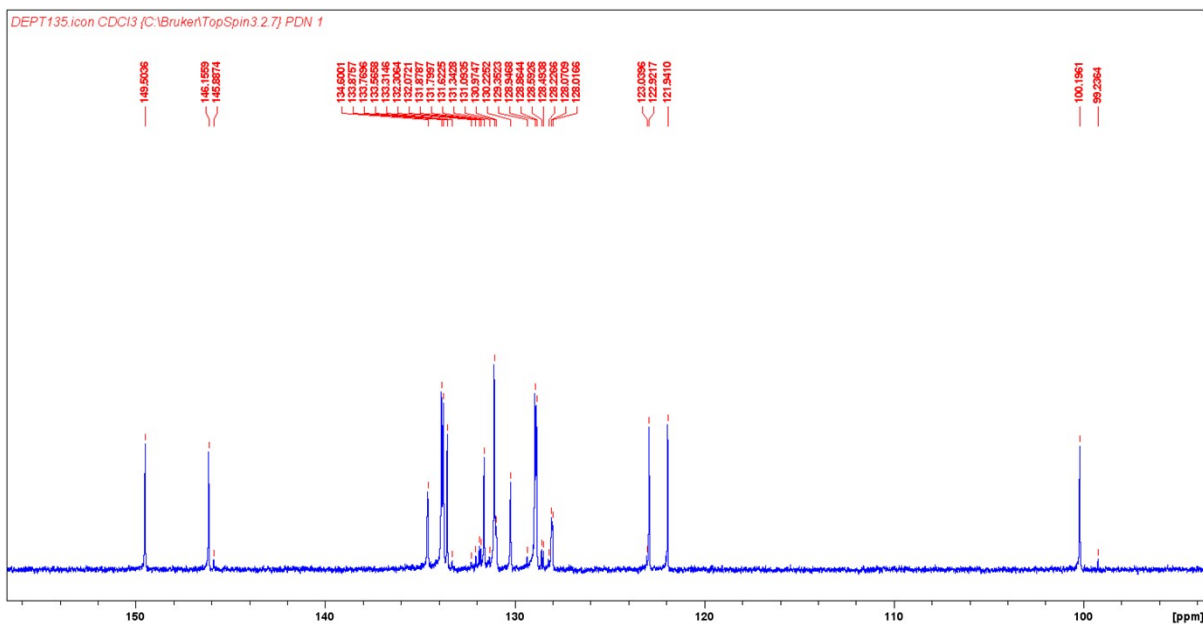
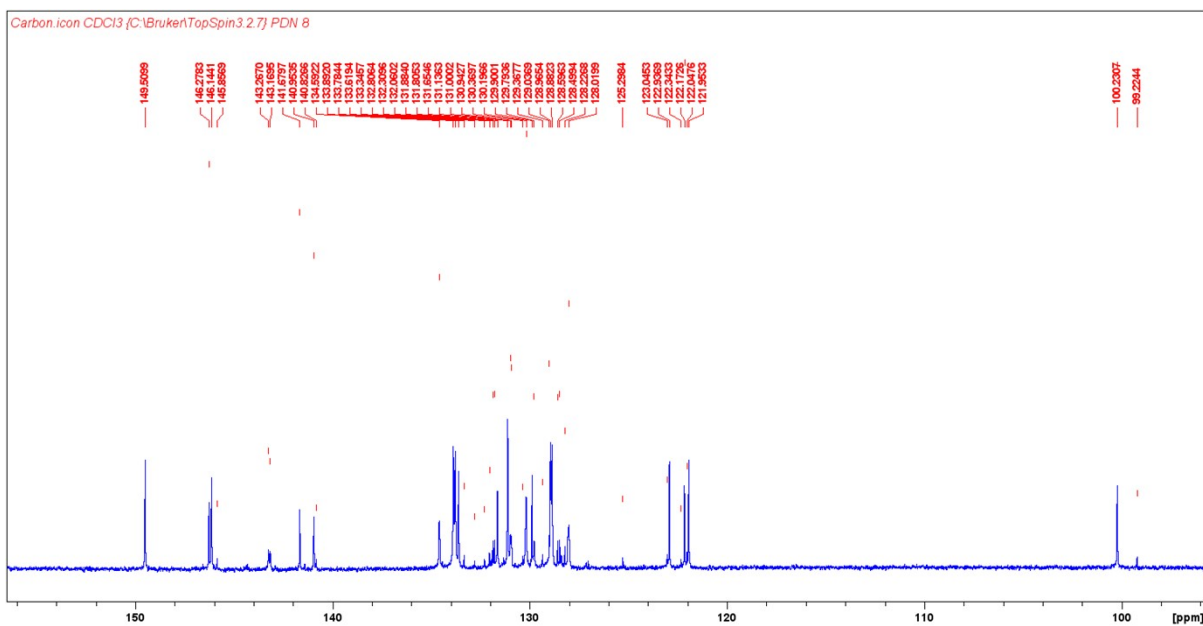


Figure S73. ¹³C{¹H} NMR spectra of AuL2 recorded at 75 MHz in CDCl₃.

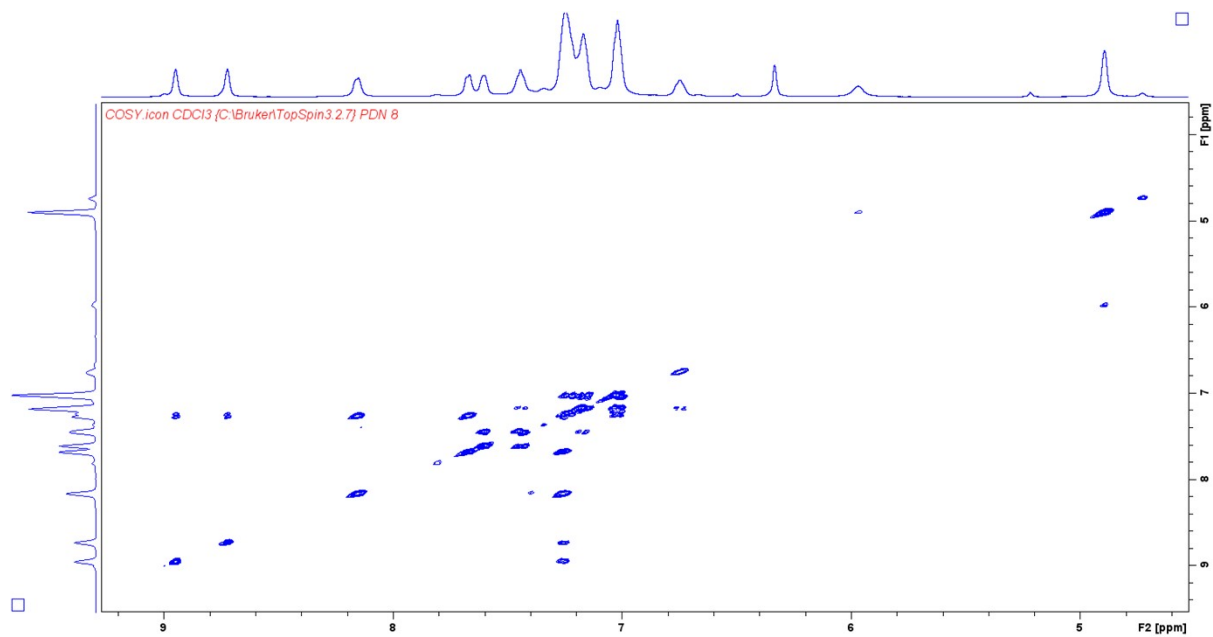


Figure S74. ^1H - ^1H COSY NMR spectrum of **AuL2** recorded at 400 MHz in CDCl_3 .

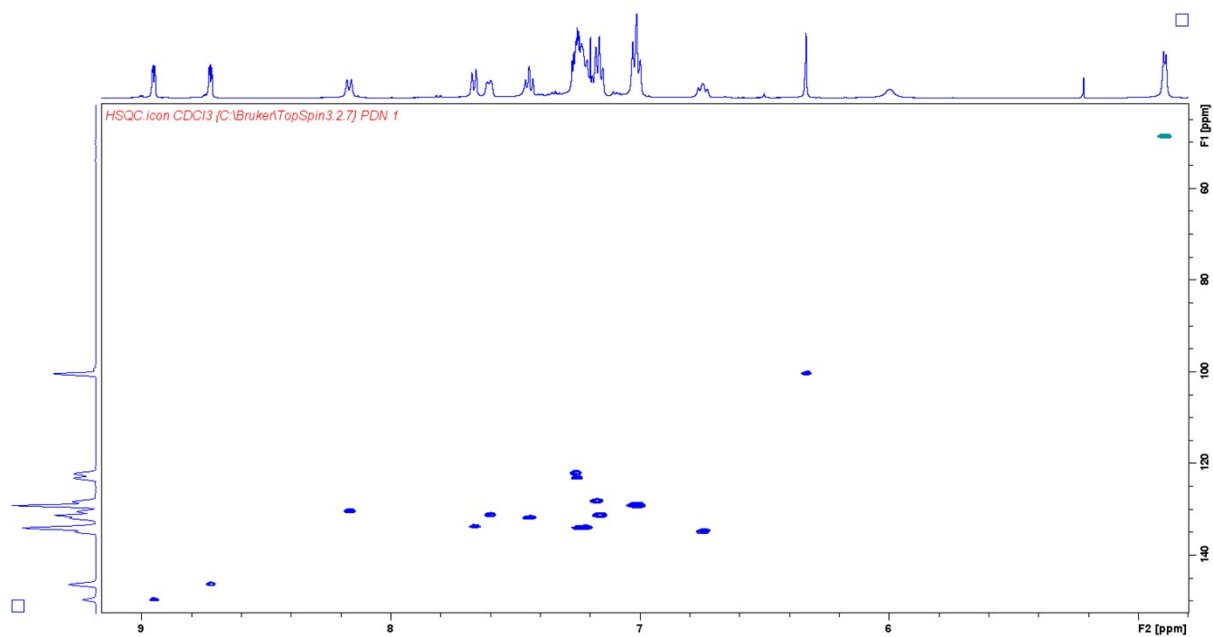


Figure S75. ^1H - ^{13}C HSQC NMR spectrum of **AuL2** recorded in CDCl_3 .

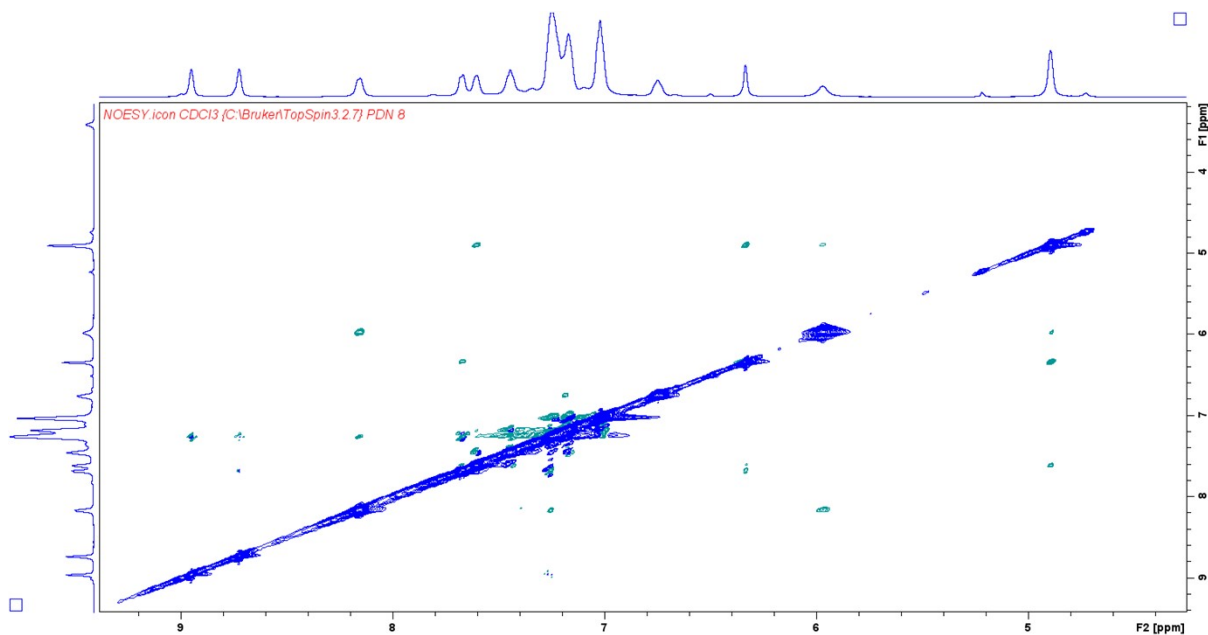
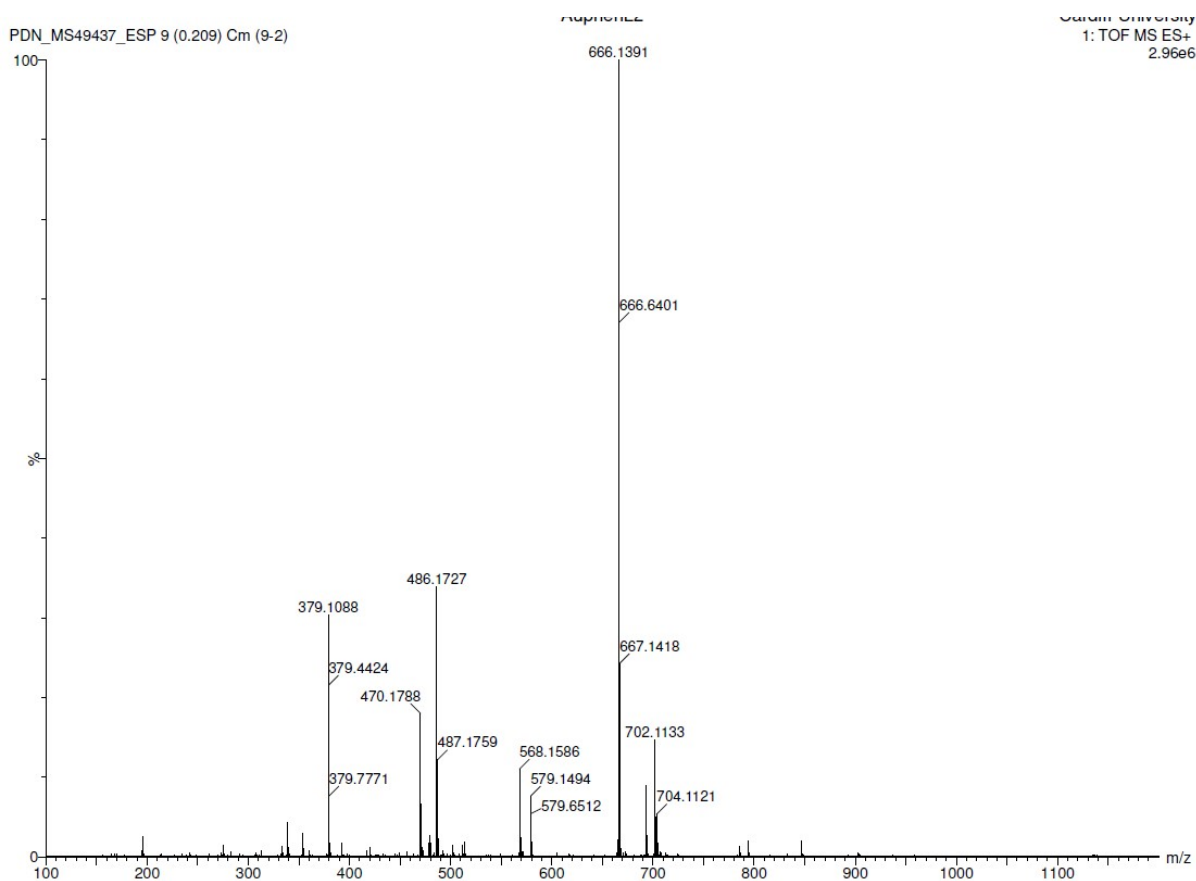


Figure S76. ^1H - ^1H NOESY NMR spectrum of **AuL2** recorded at 400 MHz in CDCl_3 .



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
666.1391	666.1373	1.8	2.7	22.5	1102.9	n/a	n/a	$\text{C}_{31}\text{H}_{24}\text{N}_3\text{P Au}$

Figure S77. HRMS (ES^+) spectrum of **AuL2**.

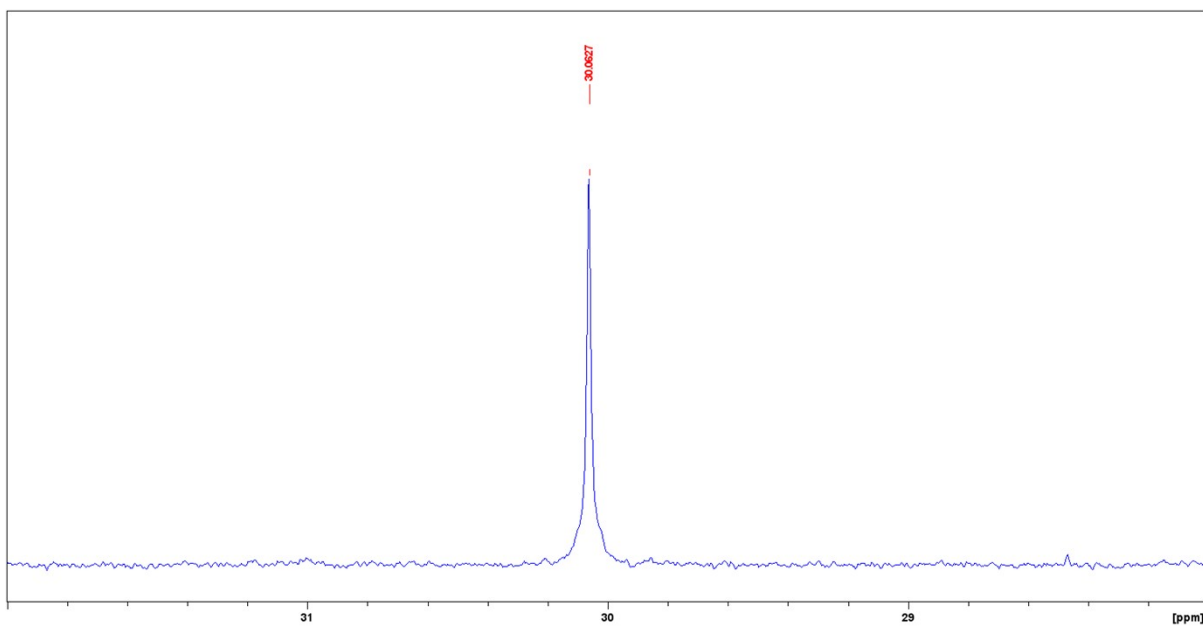


Figure S78. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of IrAuL1 recorded at 162 MHz in d_6 -acetone.

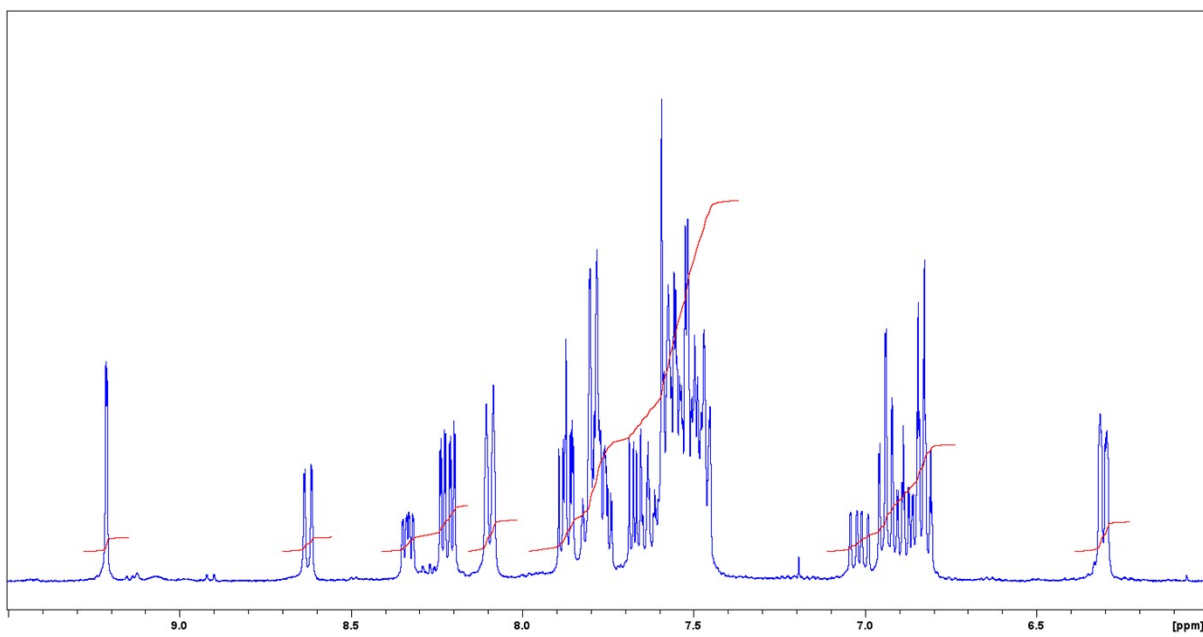


Figure S79. ^1H NMR spectra of IrAuL1 recorded at 400 MHz in d_6 -acetone.

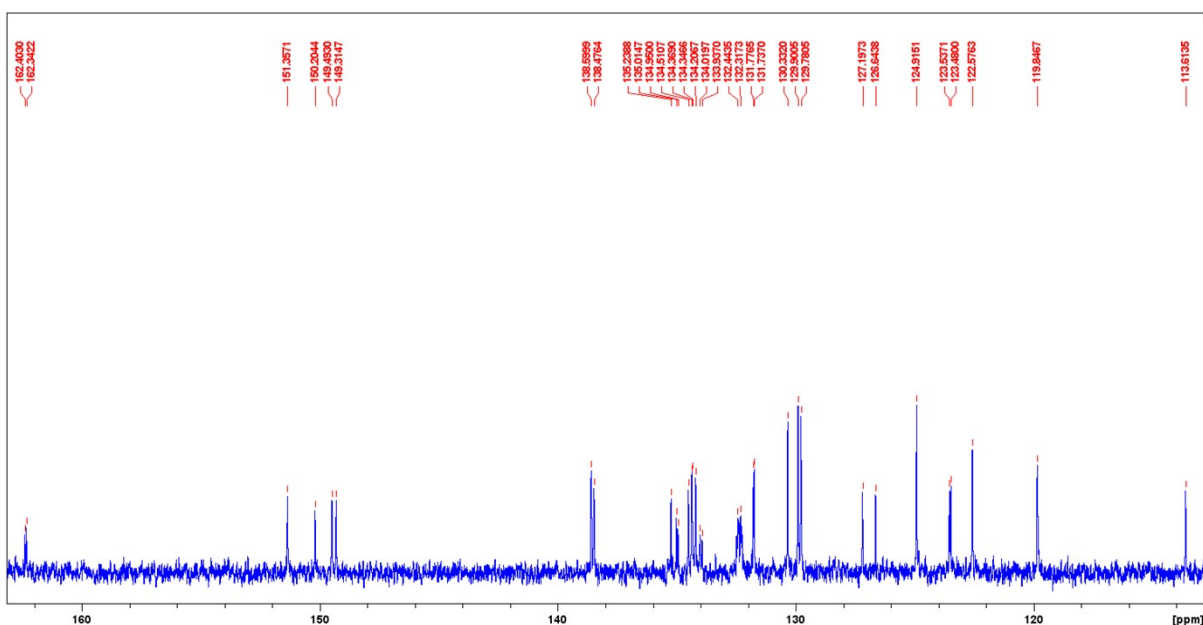
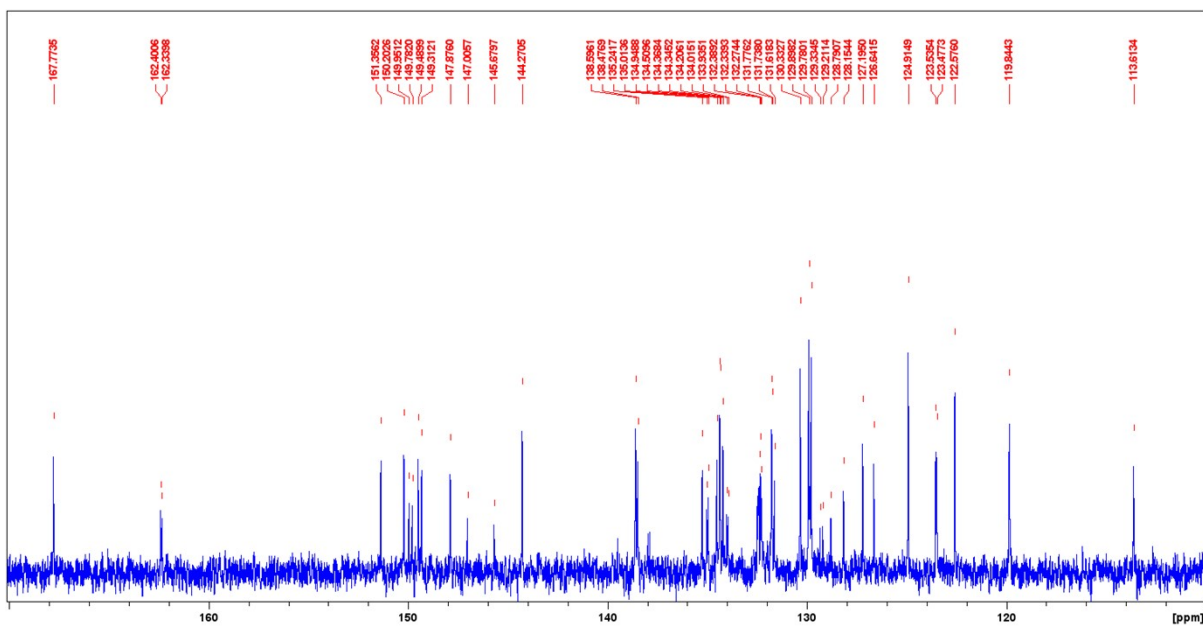


Figure S80. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of IrAuL1 recorded at 75 MHz in d_6 -acetone.

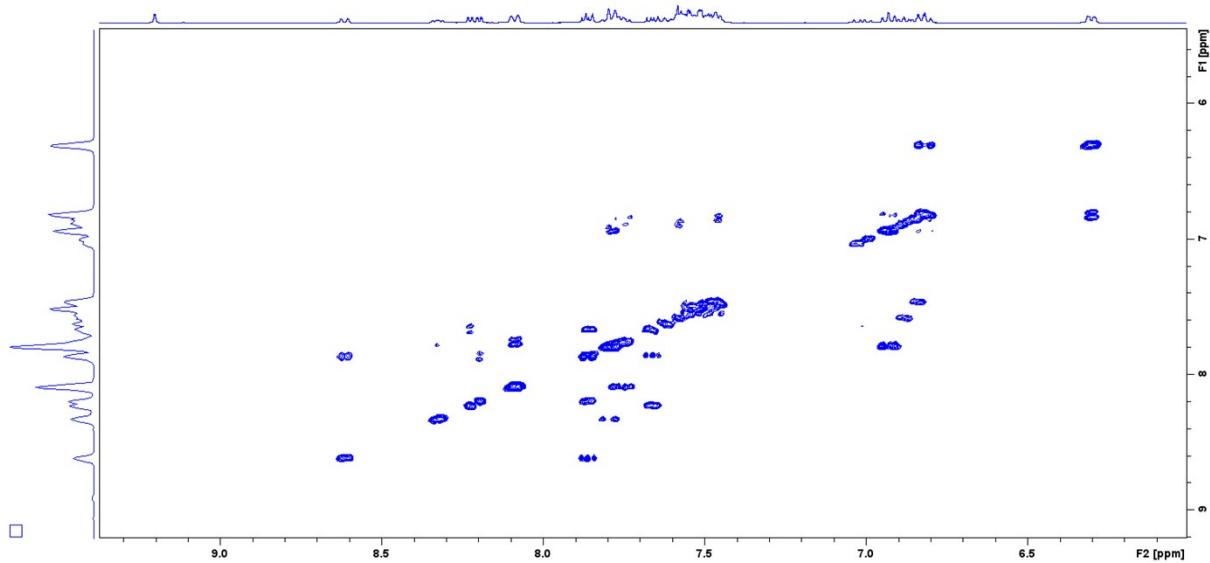


Figure S81. ^1H - ^1H COSY NMR spectrum of **IrAuL1** recorded at 400 MHz in d_6 -acetone.

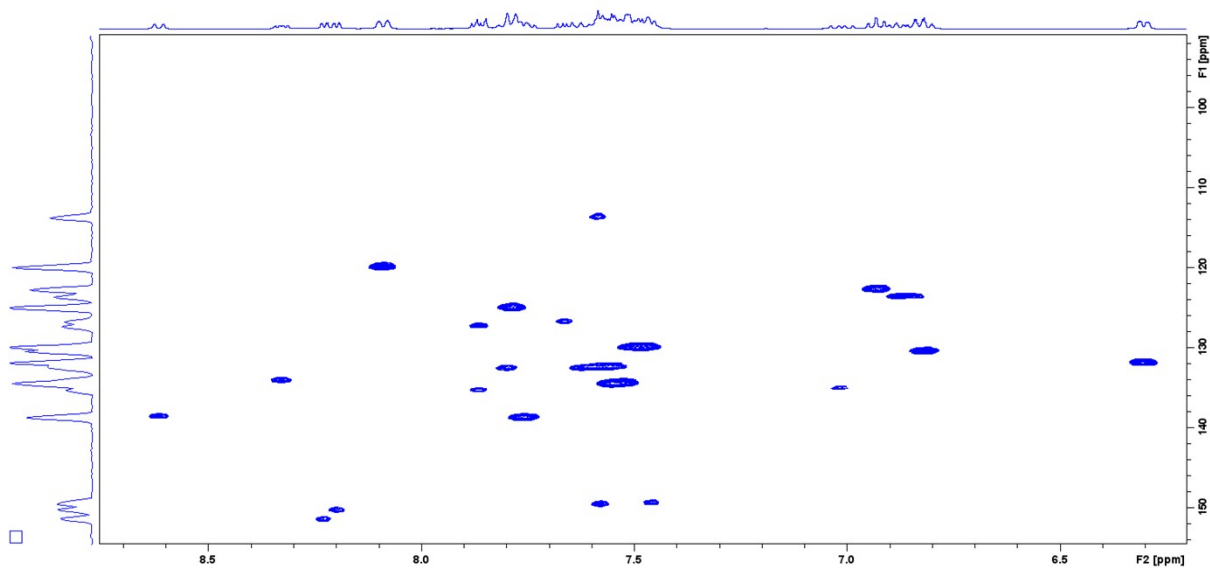


Figure S82. ^1H - ^{13}C HSQC NMR spectrum of **IrAuL1** recorded in d_6 -acetone.

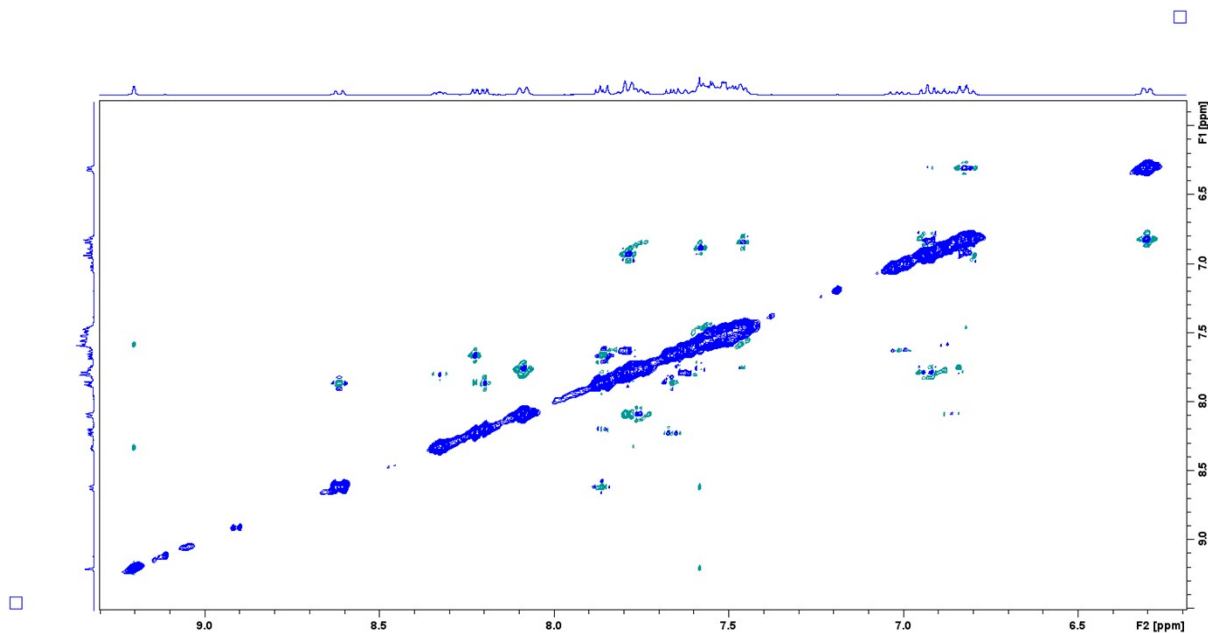
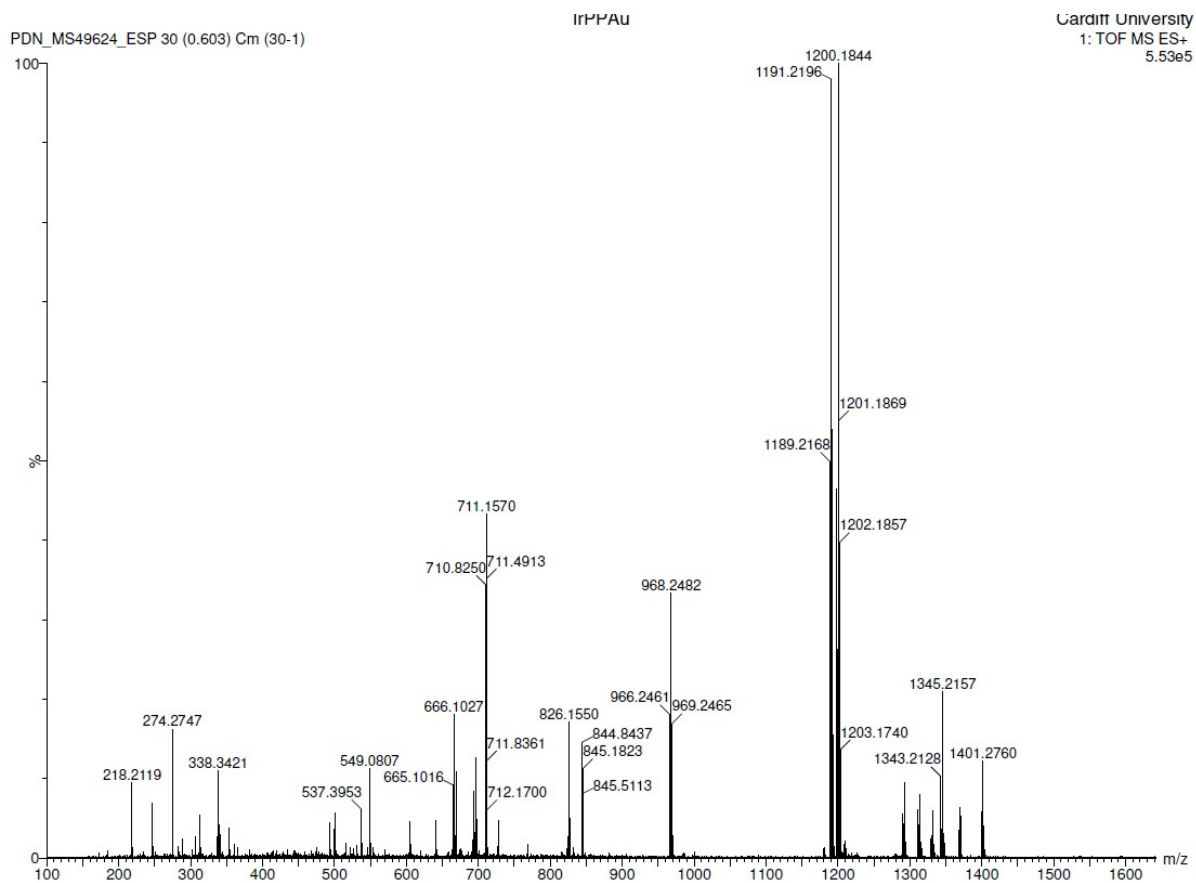


Figure S83. ^1H - ^1H NOESY NMR spectrum of IrAuL1 recorded at 400 MHz in d_6 -acetone.



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1200.1844	1200.1848	-0.4	-0.3	39.0	574.3	n/a	n/a	C53 H38 N5 Cl P Ir Au

Figure S84. HRMS (ES⁺) spectrum of IrAuL1.

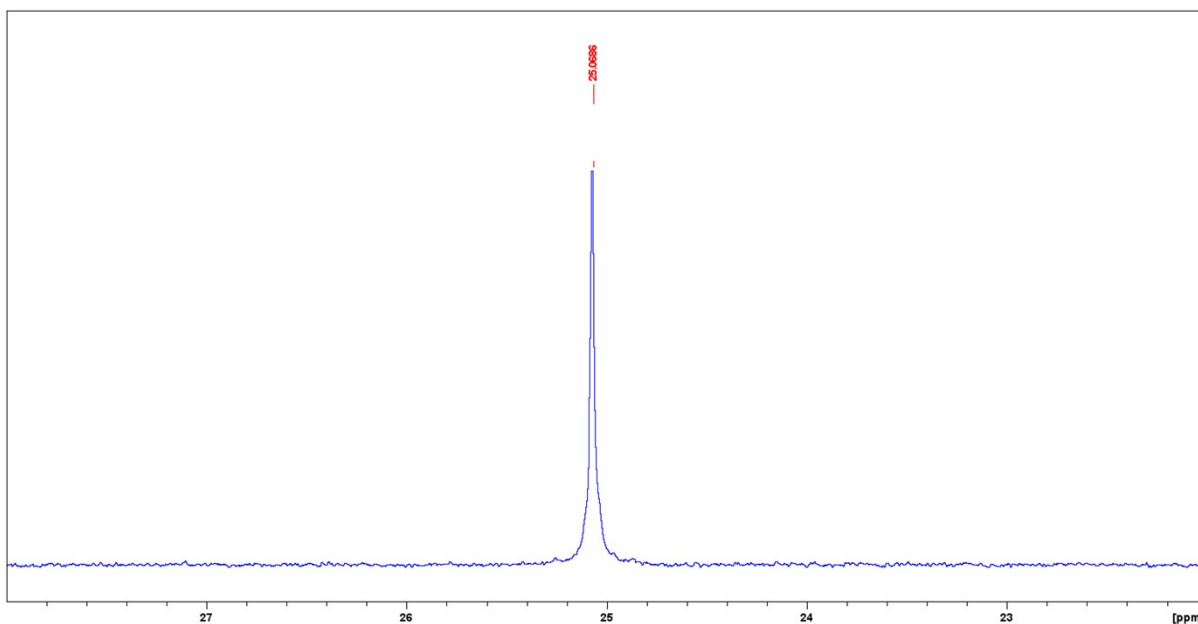


Figure S85. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of IrAuL2 recorded at 162 MHz in d_6 -acetone.

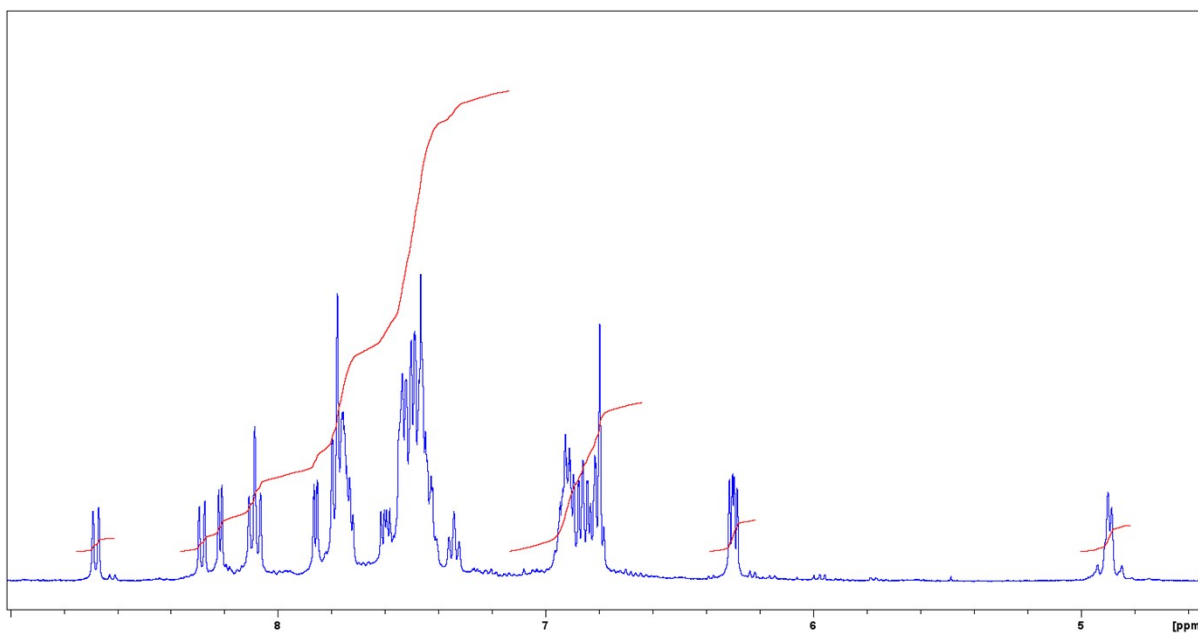


Figure S86. ^1H NMR spectra of IrAuL2 recorded at 400 MHz in d_6 -acetone.

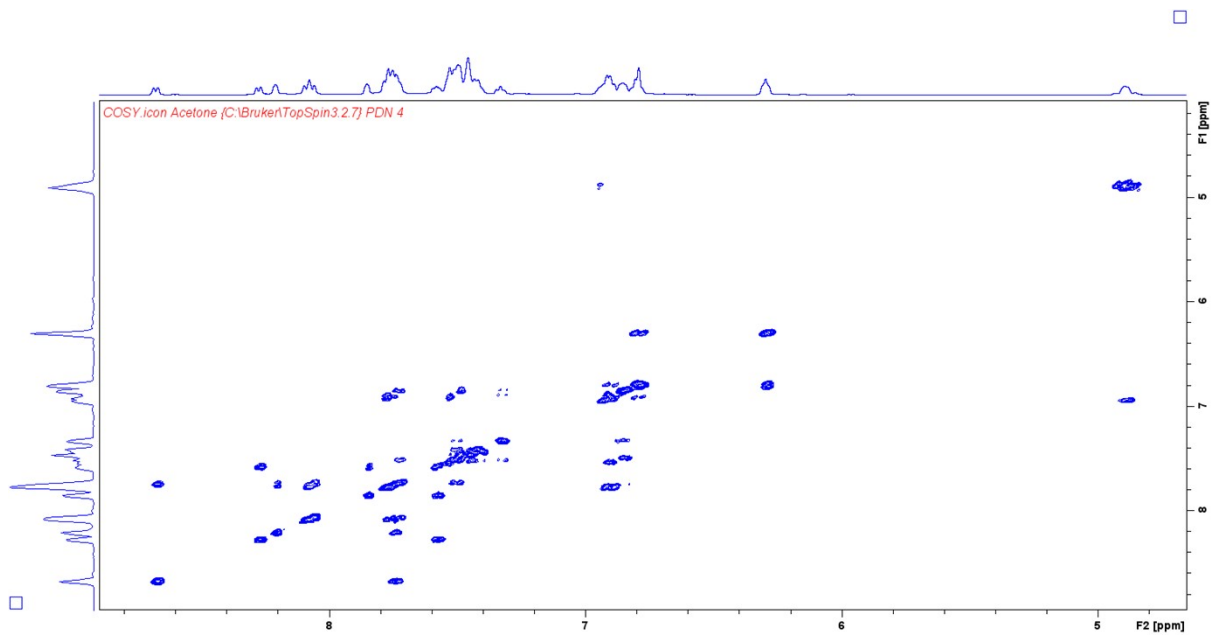


Figure S88. ¹H-¹H COSY NMR spectrum of **IrAuL2** recorded at 400 MHz in d₆-acetone.

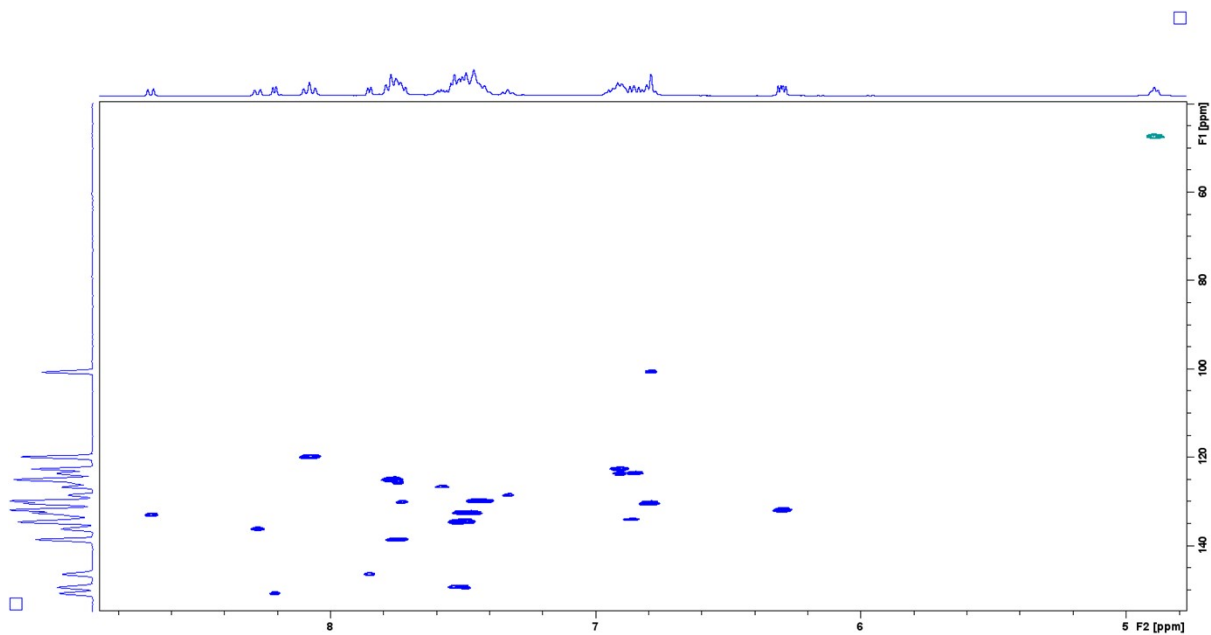


Figure S89. ¹H-¹³C HSQC NMR spectrum of **IrAuL2** recorded in d₆-acetone.

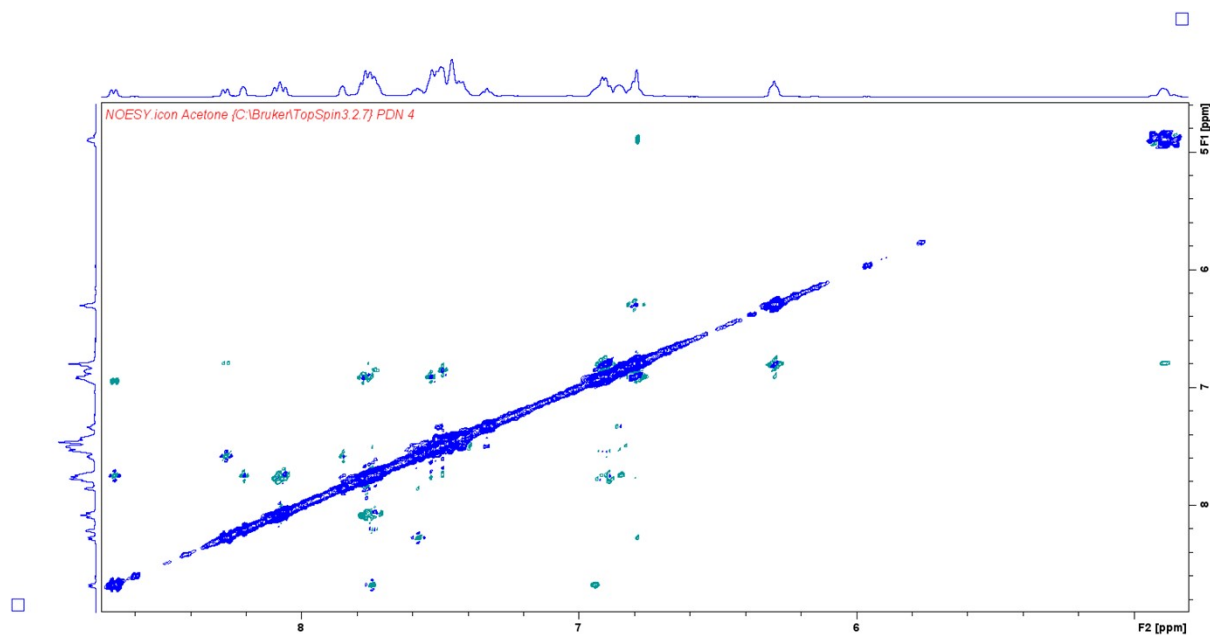
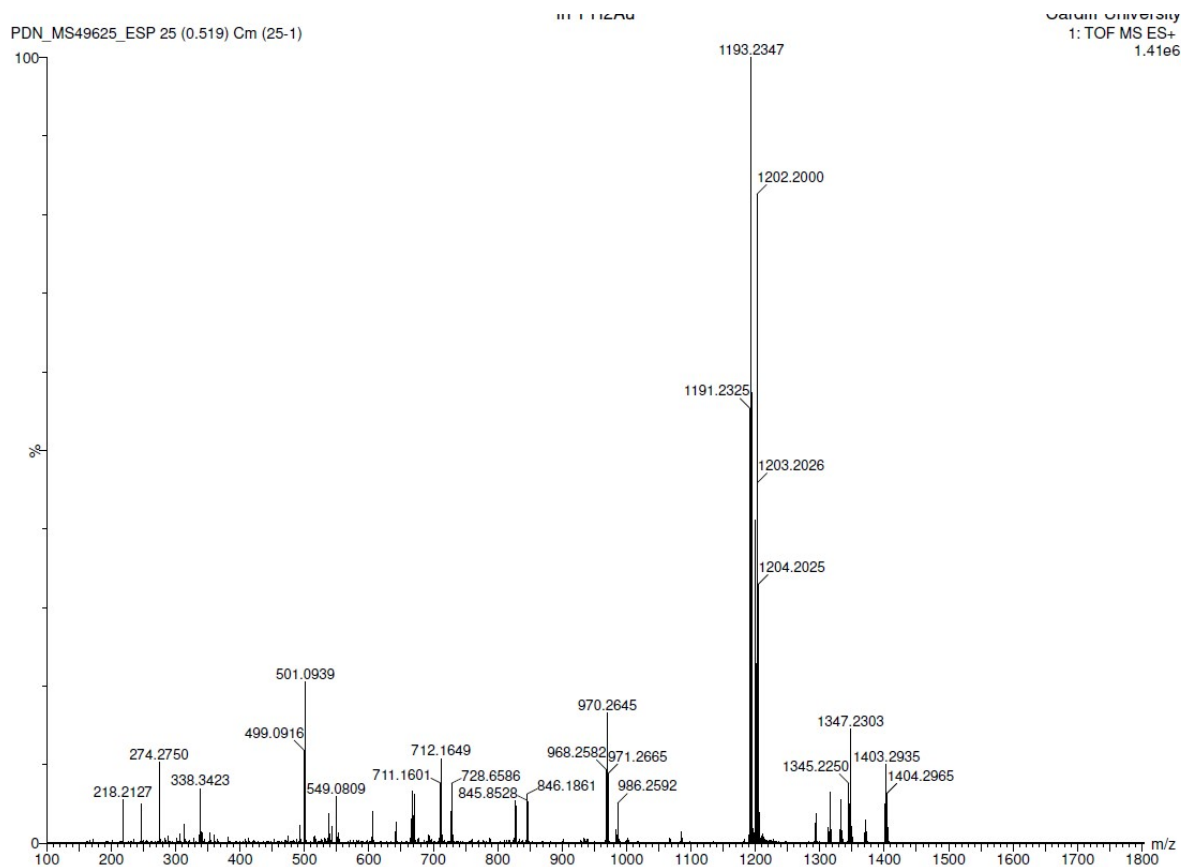


Figure S90. ^1H - ^1H NOESY NMR spectrum of IrAuL2 recorded at 400 MHz in d_6 -acetone.



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1202.2000	1202.2005	-0.5	-0.4	38.0	581.9	n/a	n/a	C ₅₃ H ₄₀ N ₅ P Cl Ir Au

Figure S91. HRMS (ES^+) spectrum of IrAuL2.

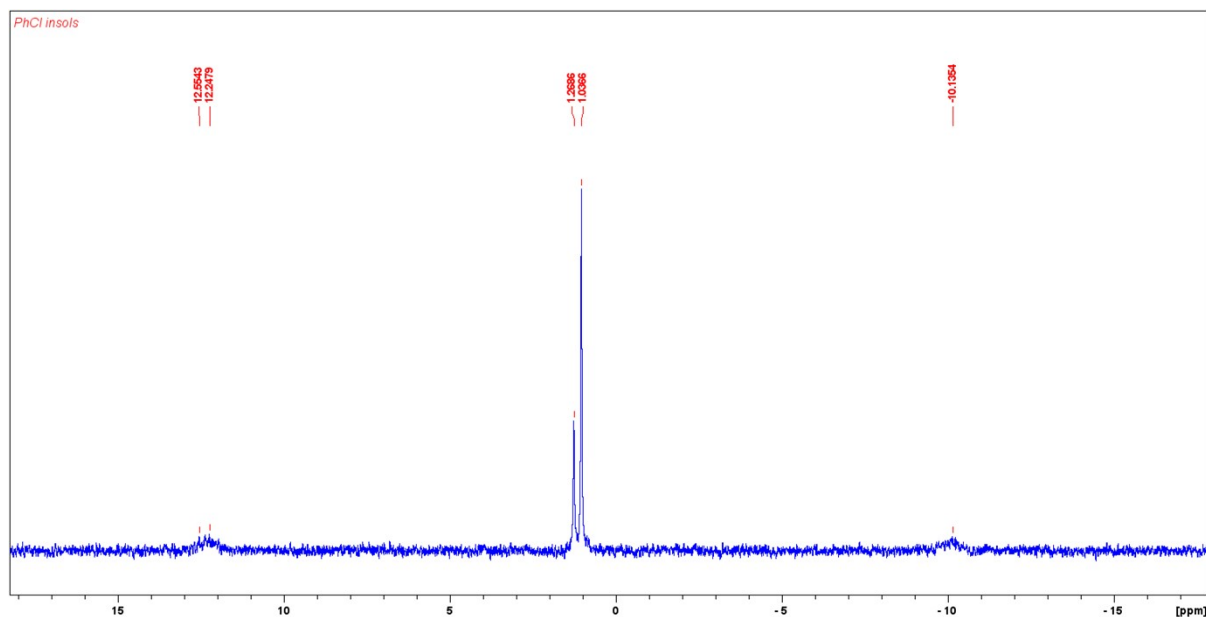


Figure S92. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **RePtL1** recorded at 293 K and 162 MHz in d_6 -dmso.

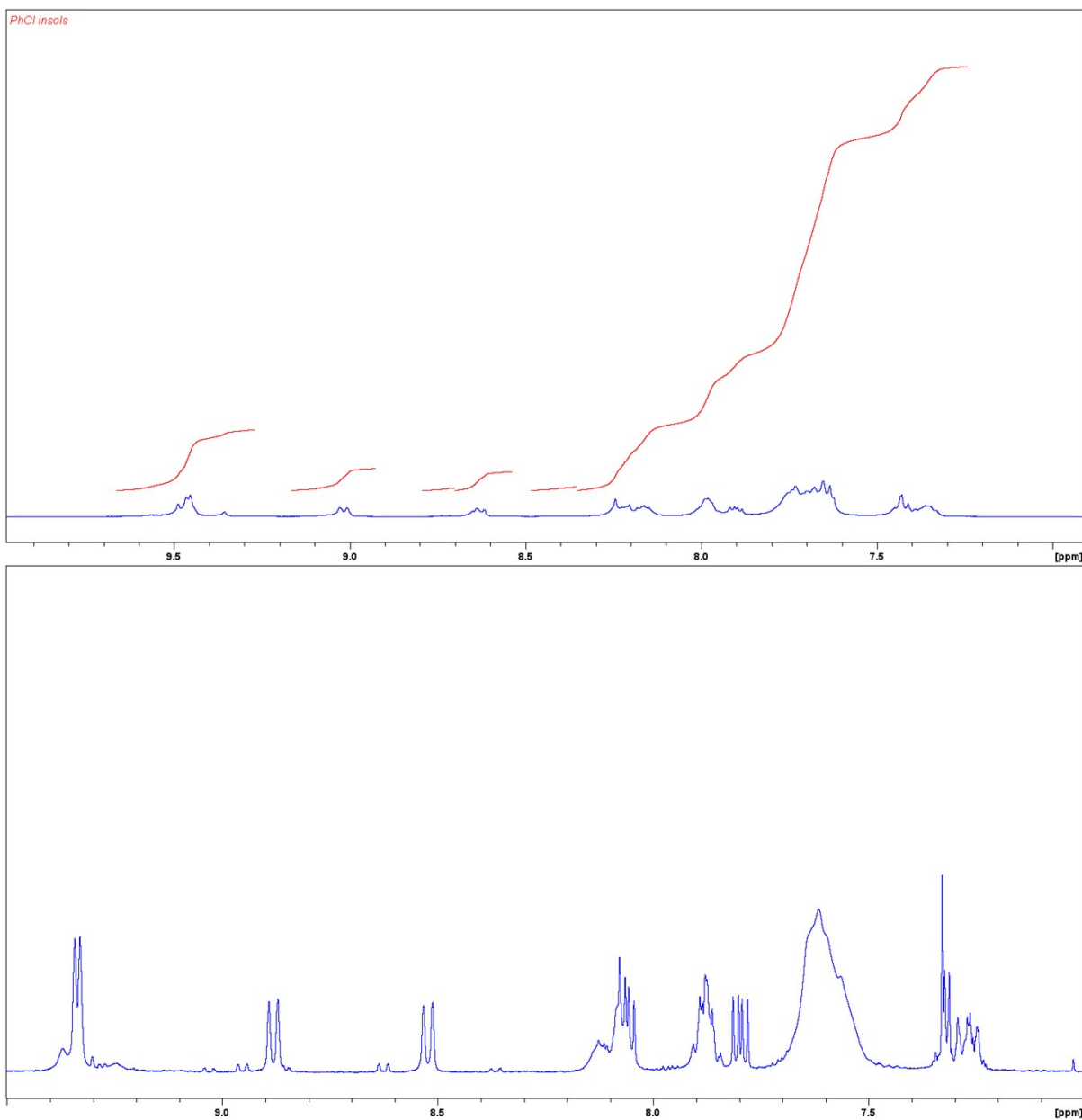


Figure S93. ^1H NMR spectra of **RePtL1** recorded at 400 MHz in $\text{d}_6\text{-dmsol}$. Upper trace recorded at 293 K and lower trace at 353 K.

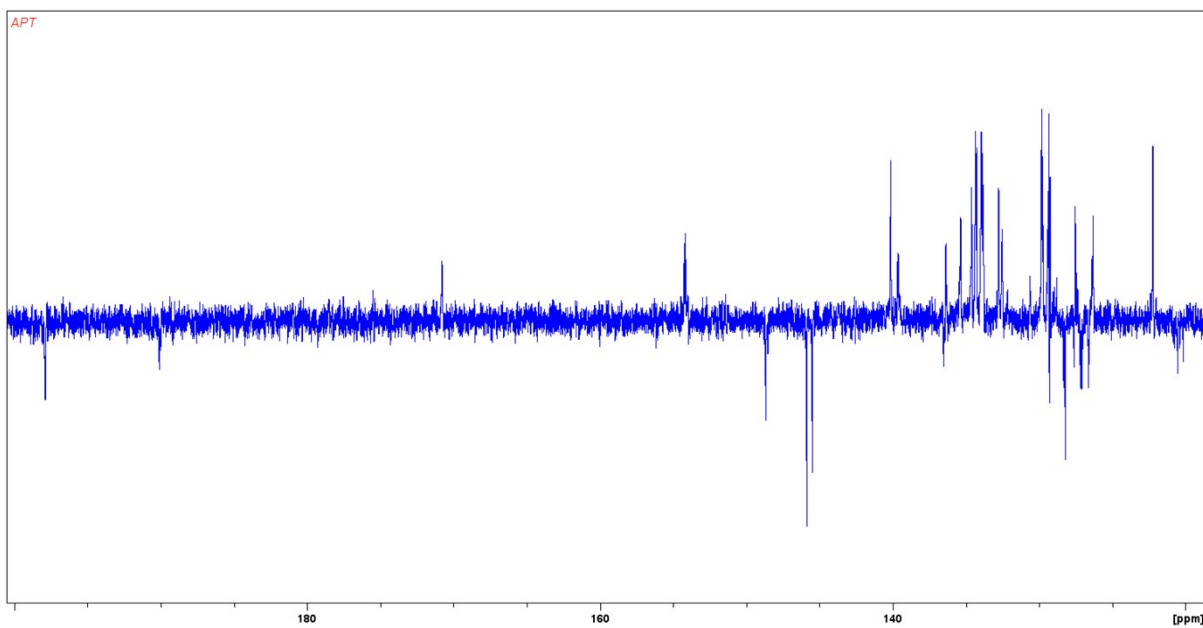


Figure S94. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **RePtL1** recorded at 75 MHz in $\text{d}_6\text{-dmsol}$.

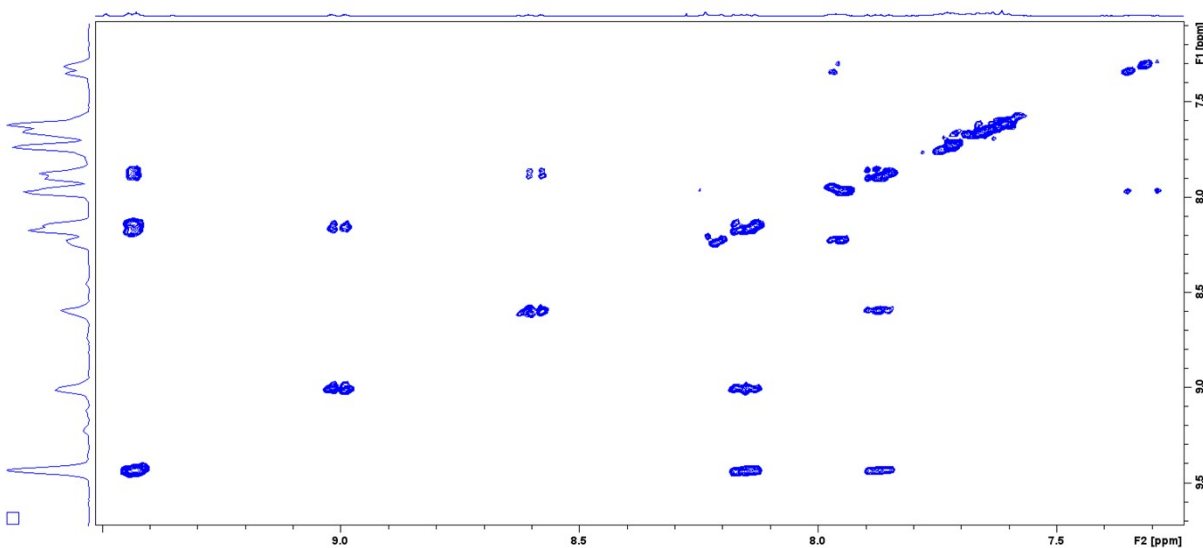


Figure S95. $^1\text{H}\text{-}^1\text{H}$ COSY NMR spectrum of **RePtL1** recorded at 400 MHz in $\text{d}_6\text{-dmsol}$.

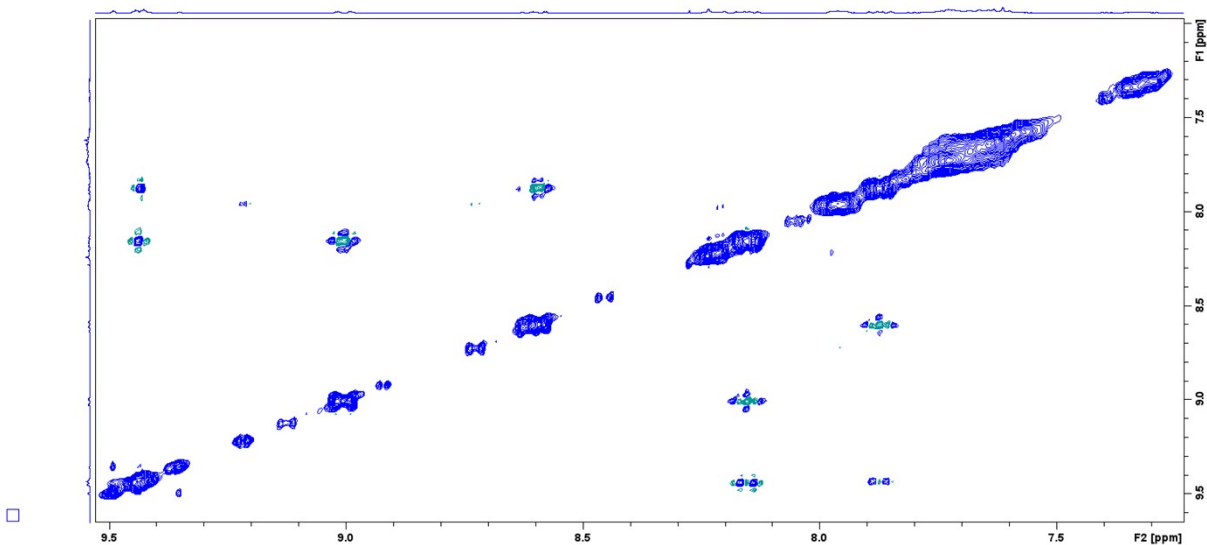
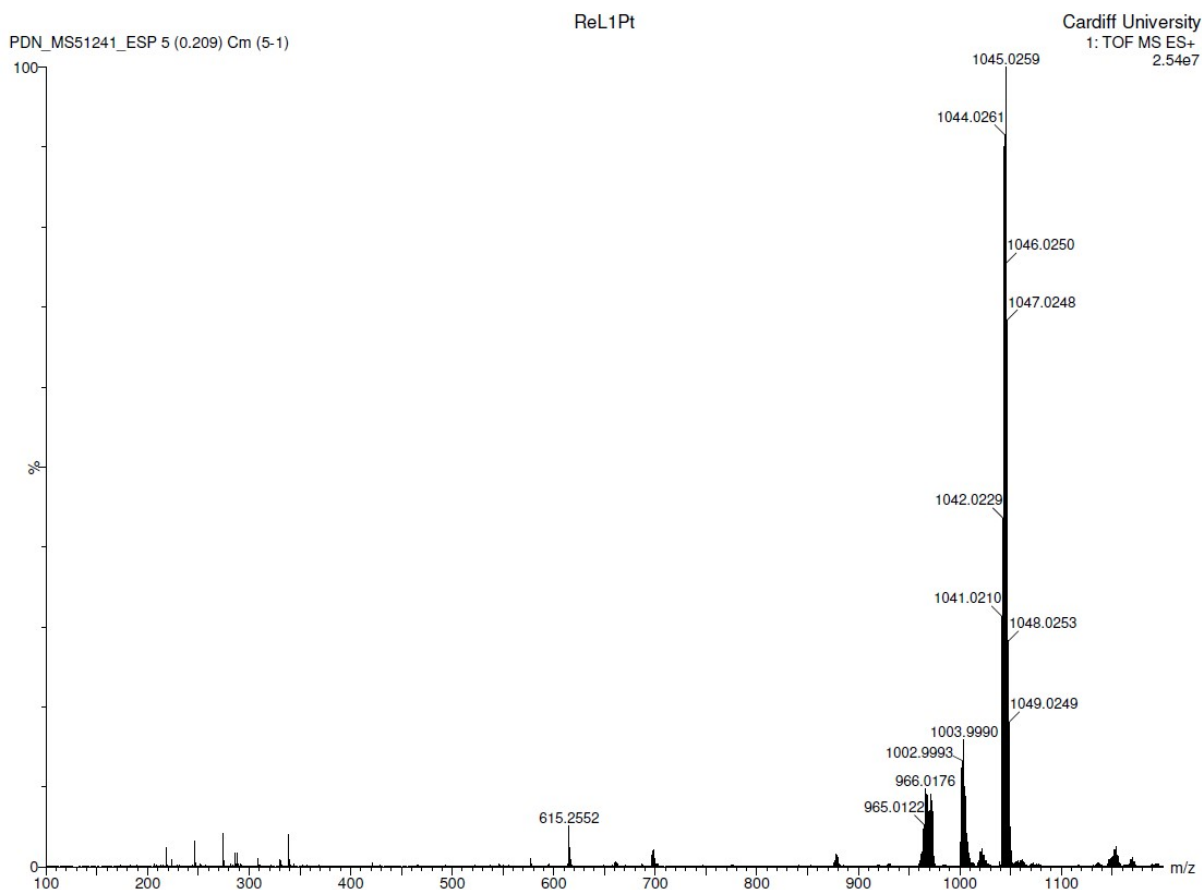


Figure S96. ^1H - ^1H NOESY NMR spectrum of **RePtL1** recorded at 400 MHz in d_6 -dmsO.



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1003.9990	1003.9983	0.7	0.7	26.0	1112.2	n/a	n/a	C34 H22 N3 O3 P C12 187Re 196Pt

Figure S97. HRMS (ES^+) spectrum of **RePtL1**.

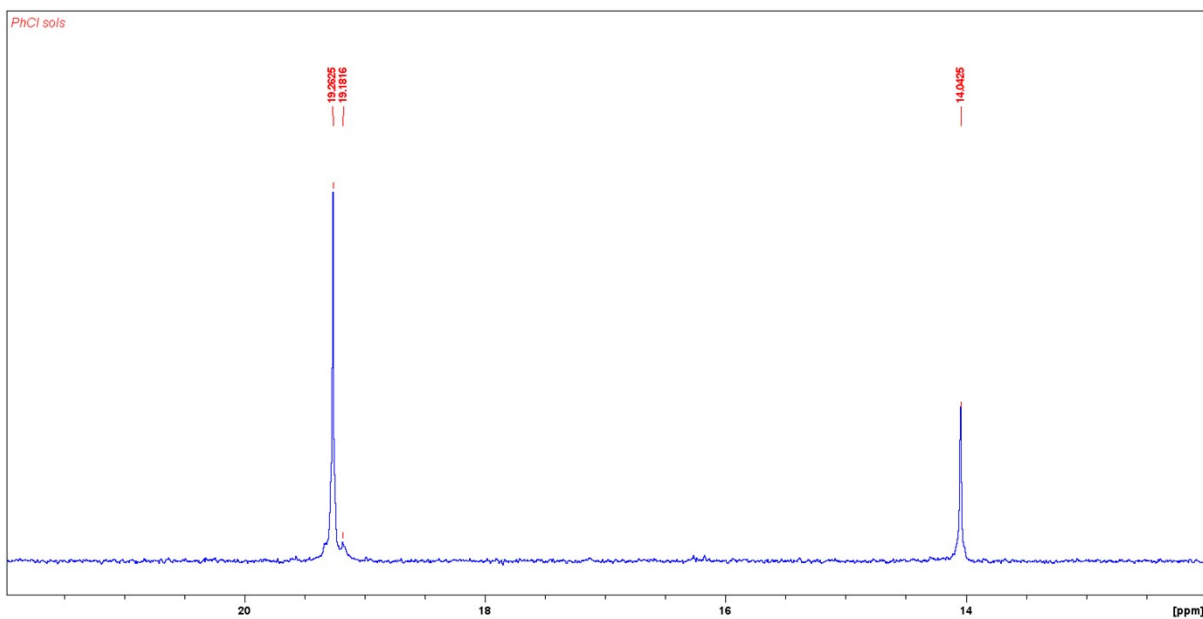


Figure S98. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **RePdL1** recorded at 162 MHz in CDCl_3 .

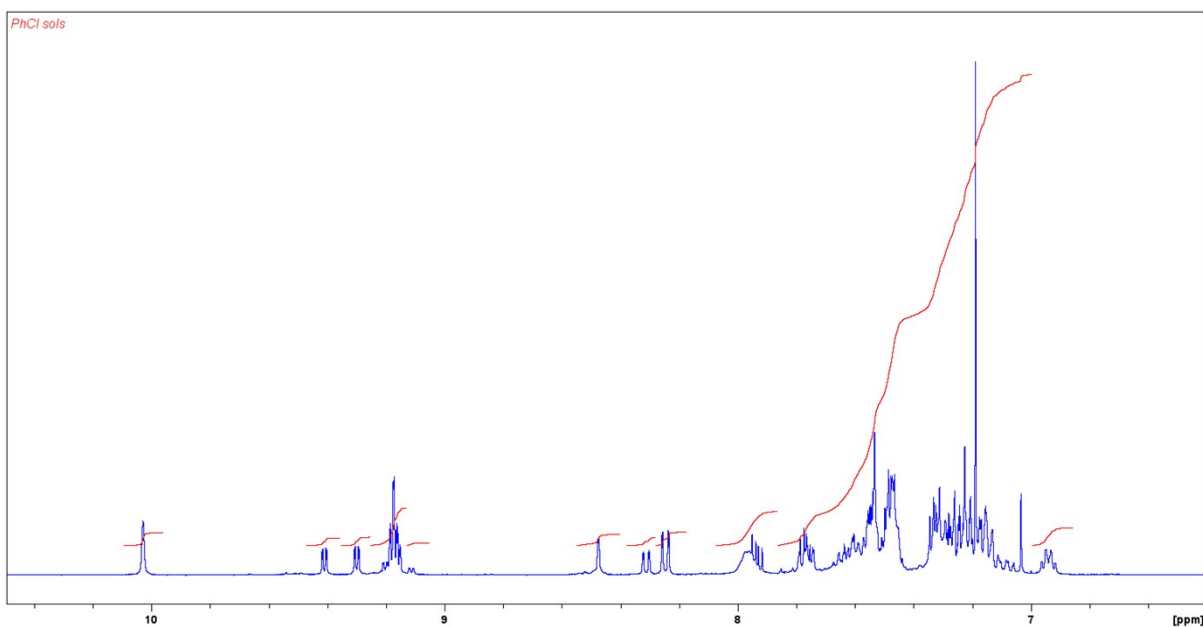


Figure S99. ^1H NMR spectra of **RePdL1** recorded at 400 MHz in CDCl_3 .

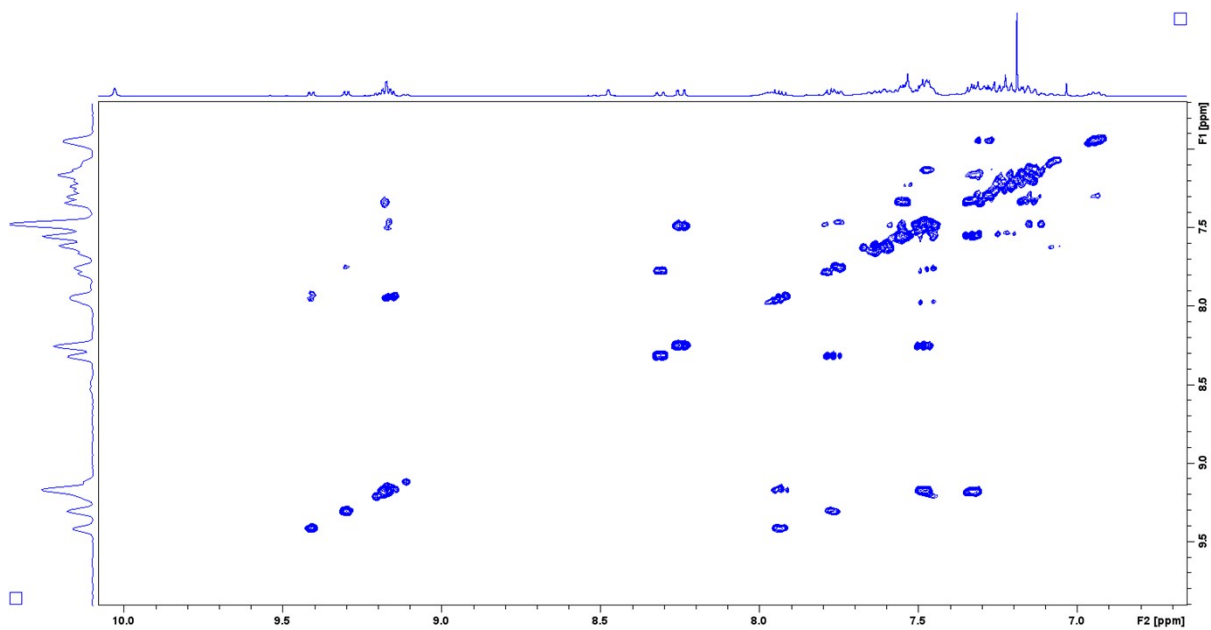


Figure S100. ¹H-¹H COSY NMR spectrum of **RePdL1** recorded at 400 MHz in CDCl₃.

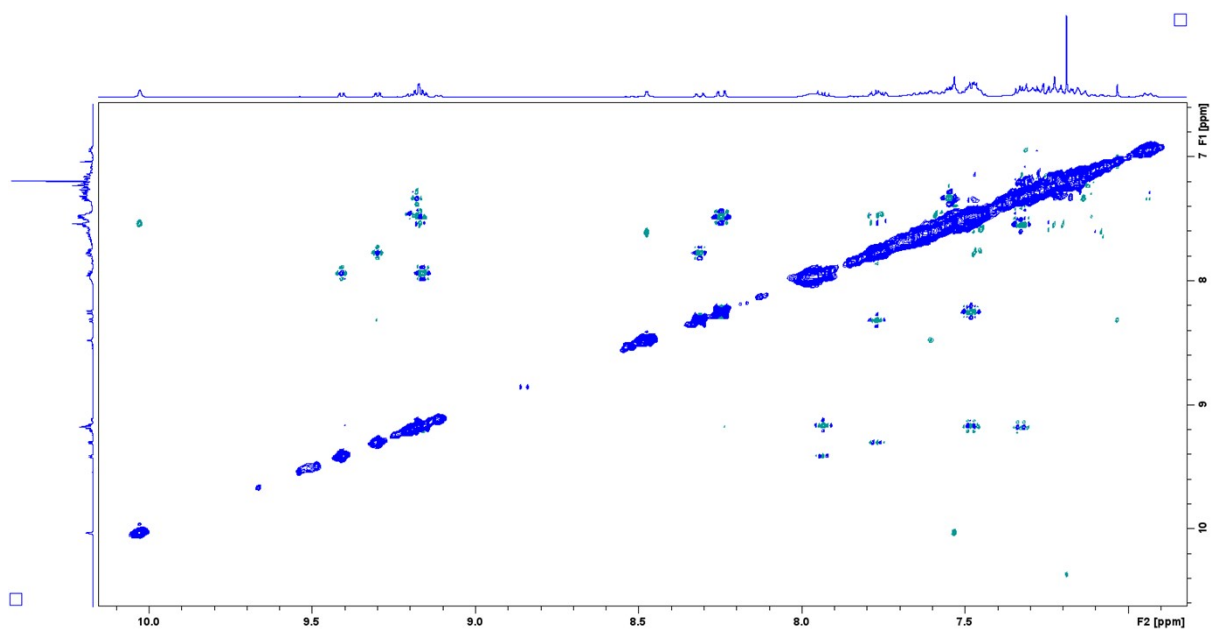


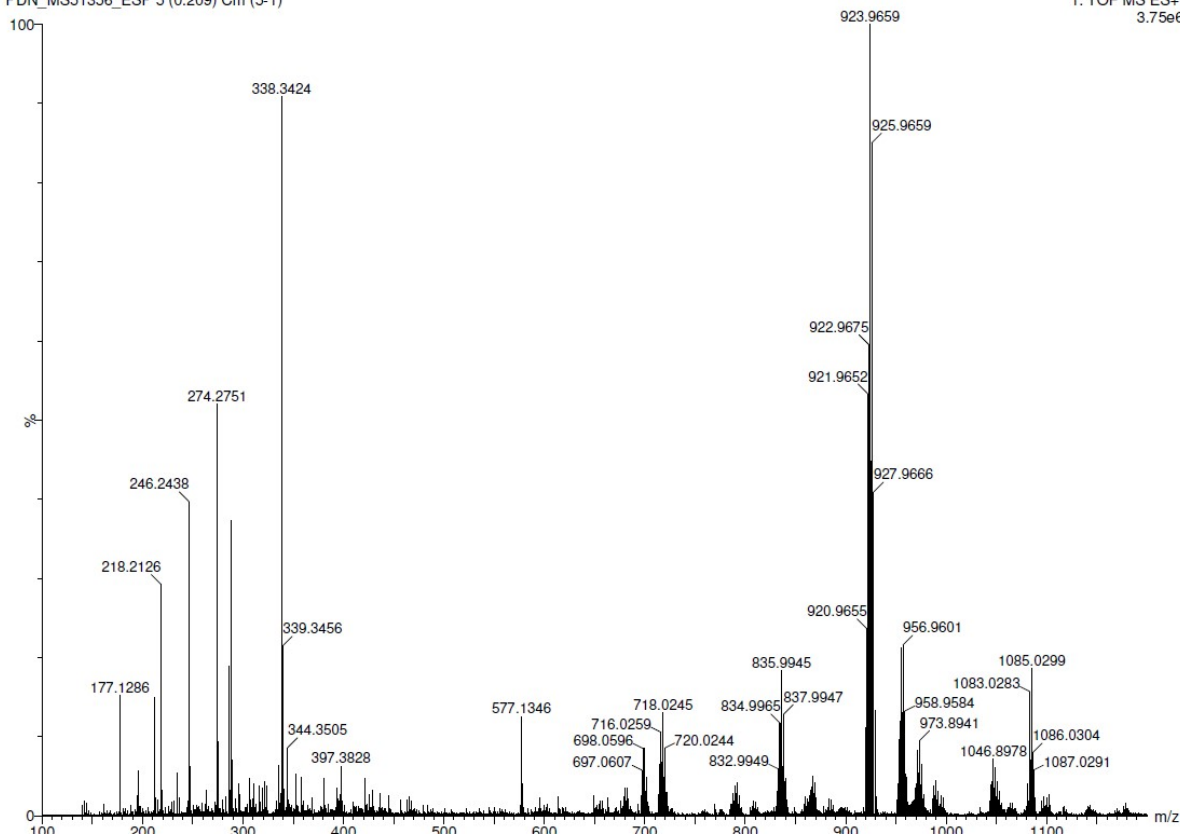
Figure S101. ¹H-¹H NOESY NMR spectrum of **RePdL1** recorded at 400 MHz in CDCl₃.

04-Jun-2024

RePdppt

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
3.75e6

PDN_MS51356_ESP 5 (0.209) Cm (5-1)



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
923.9659	923.9656	0.3	0.3	26.0	1207.5	n/a	n/a	C35 H23 N3 O5 P Cl Pd Re

Figure S102. HRMS (ES⁺) spectrum of RePdL1.

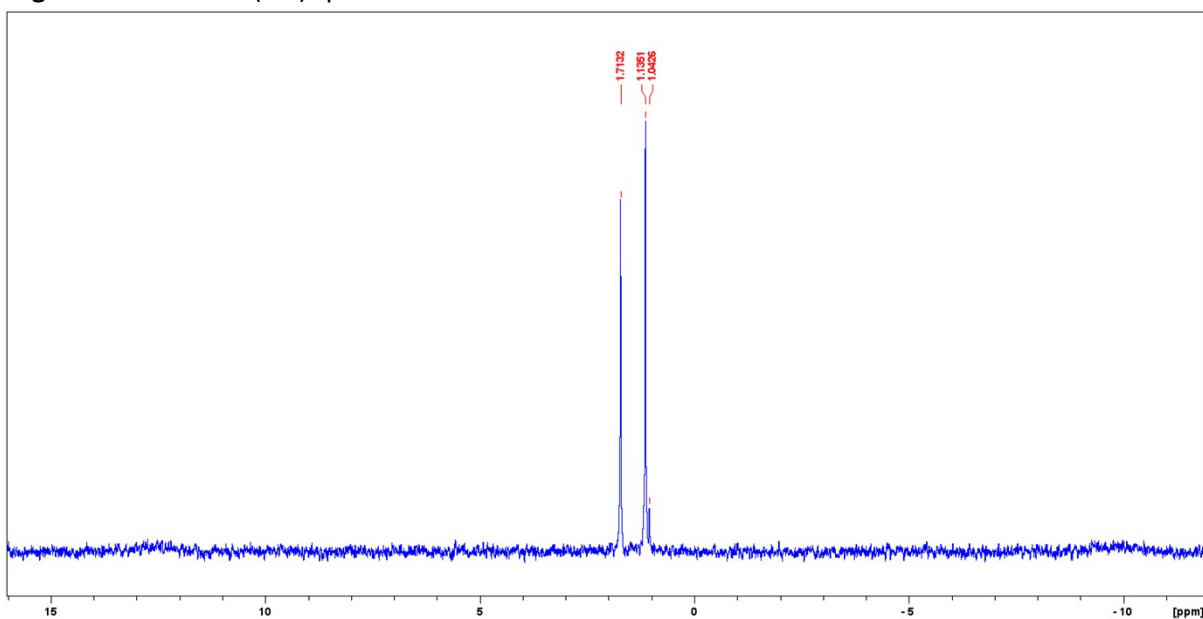


Figure S103. ³¹P{¹H} NMR spectrum of IrPtL1 recorded at 162 MHz in d₆-dmsO.

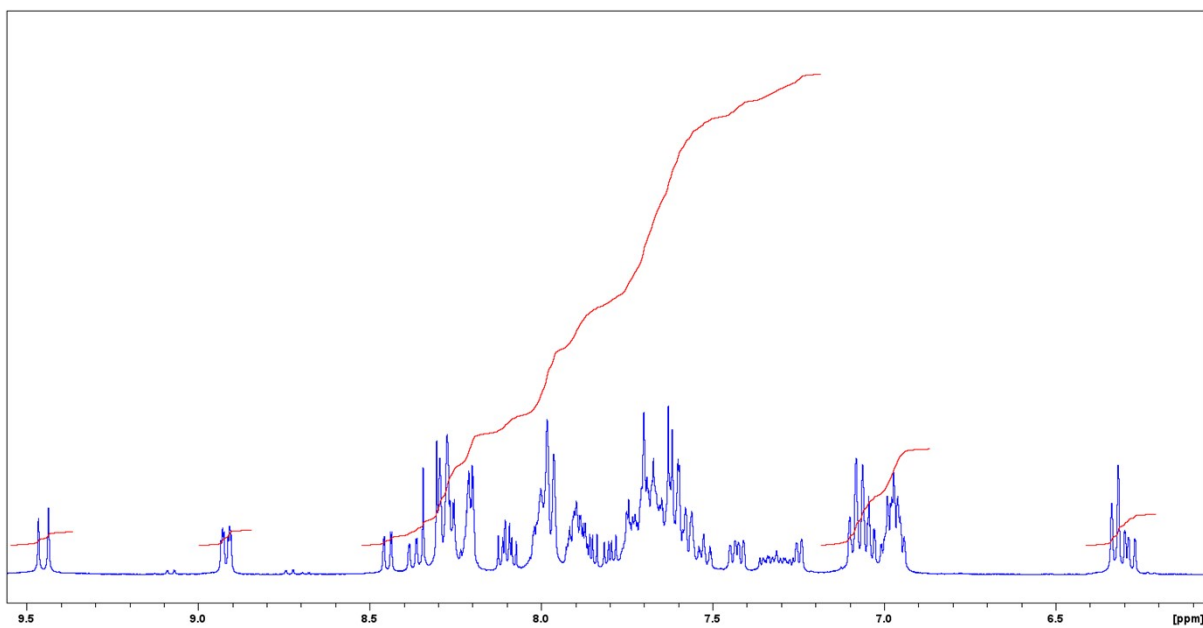


Figure S104. ^1H NMR spectra of **IrPtL1** recorded at 400 MHz in d_6 -dmsol.

□

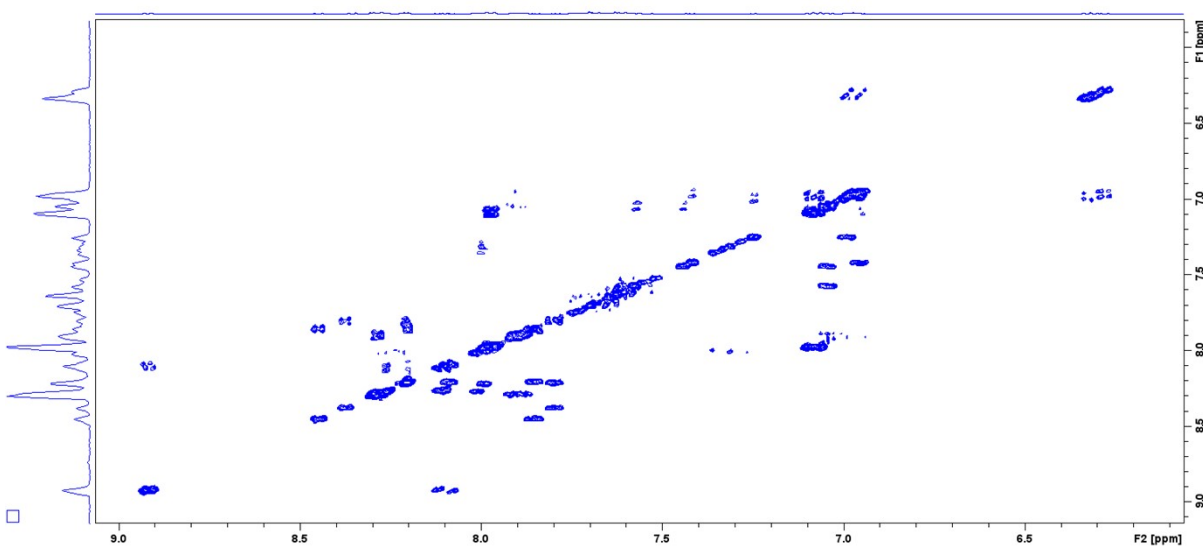


Figure S105. ^1H - ^1H COSY NMR spectrum of **IrPtL1** recorded at 400 MHz in d_6 -dmsol.

□

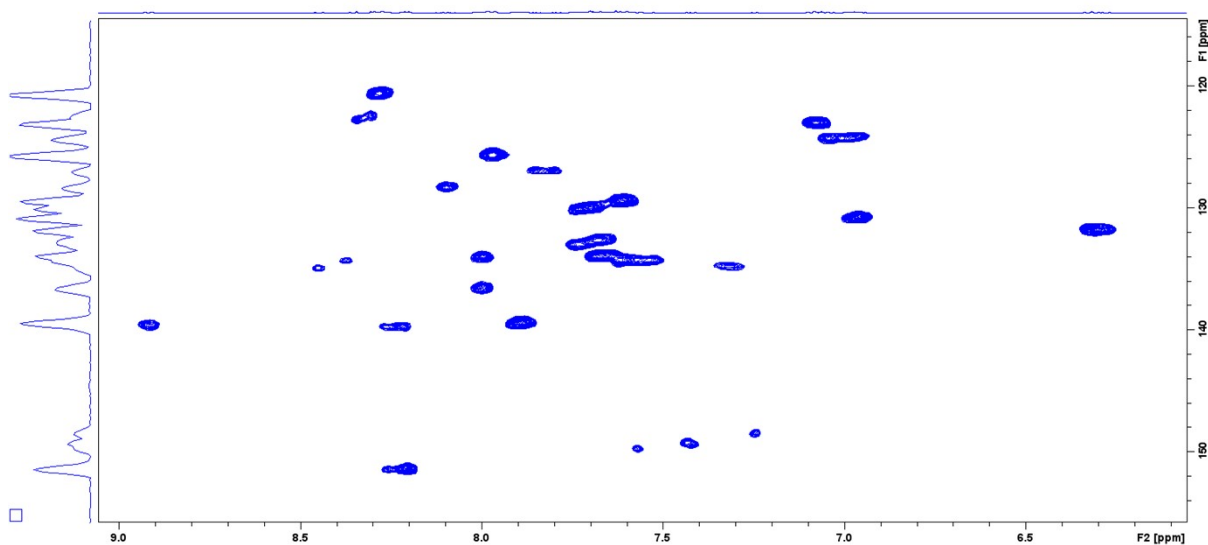


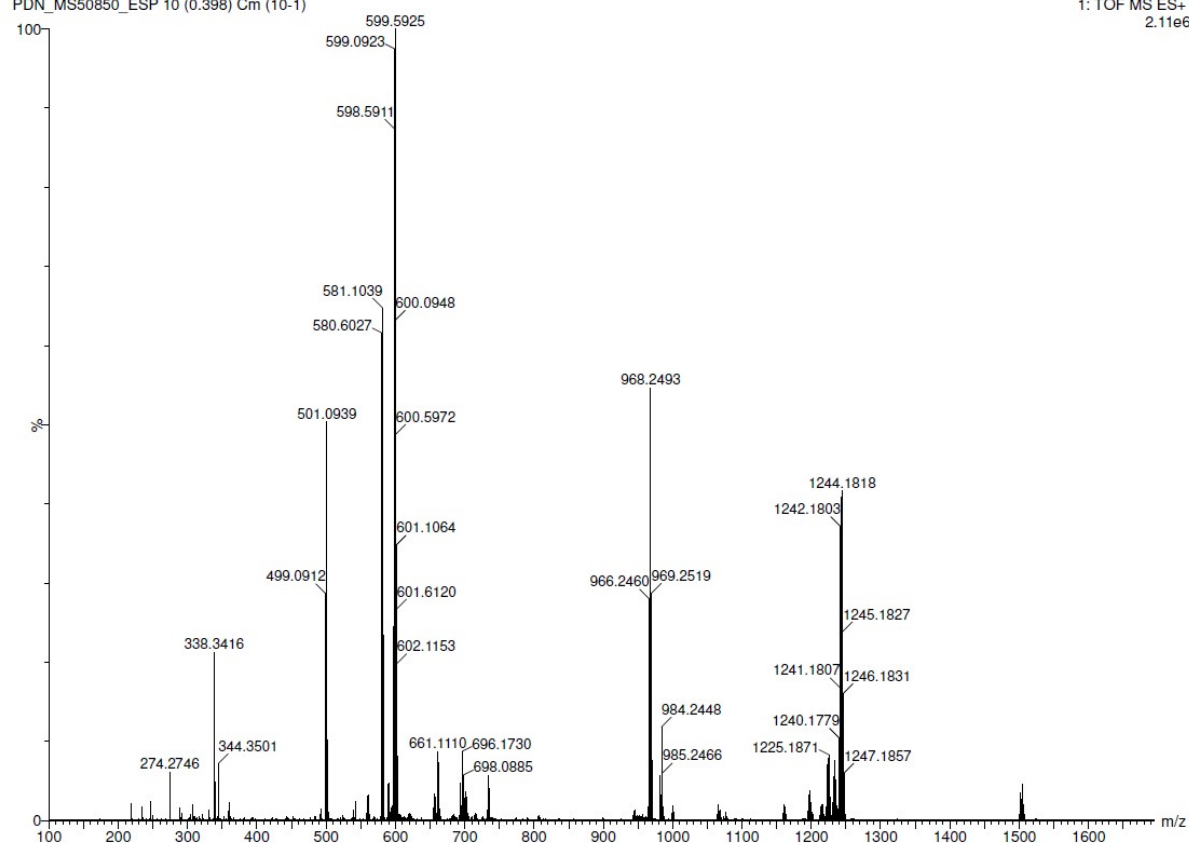
Figure S106. ^1H - ^{13}C HSQC NMR spectrum of IrPtL1 recorded in d_6 -dmso.

30-Apr-2024

IrL1Pt

XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
2.11e6

PDN_MS50850_ESP 10 (0.398) Cm (10-1)



Minimum: -1.5
Maximum: 5.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1233.1541	1233.1519	2.2	1.8	39.0	589.1	n/a	n/a	C53 H38 N5 P C12 Ir Pt

Figure S107. HRMS (ES^+) spectrum of IrPtL1.

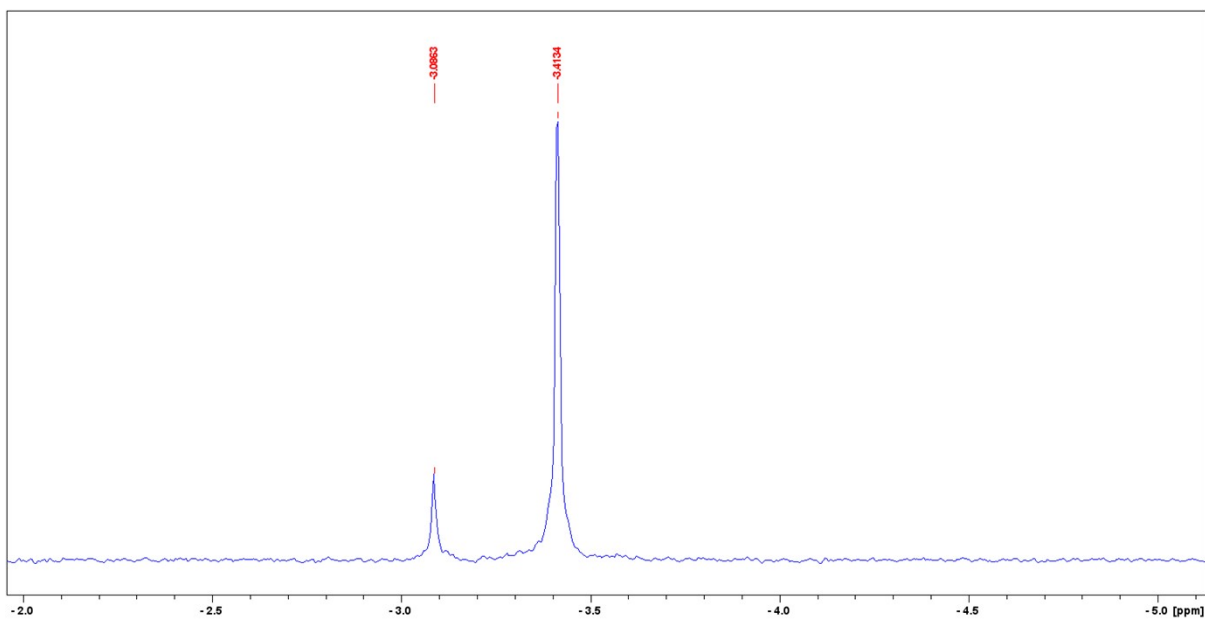


Figure S108. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of IrPdL1 recorded at 162 MHz in d_6 -dmso.

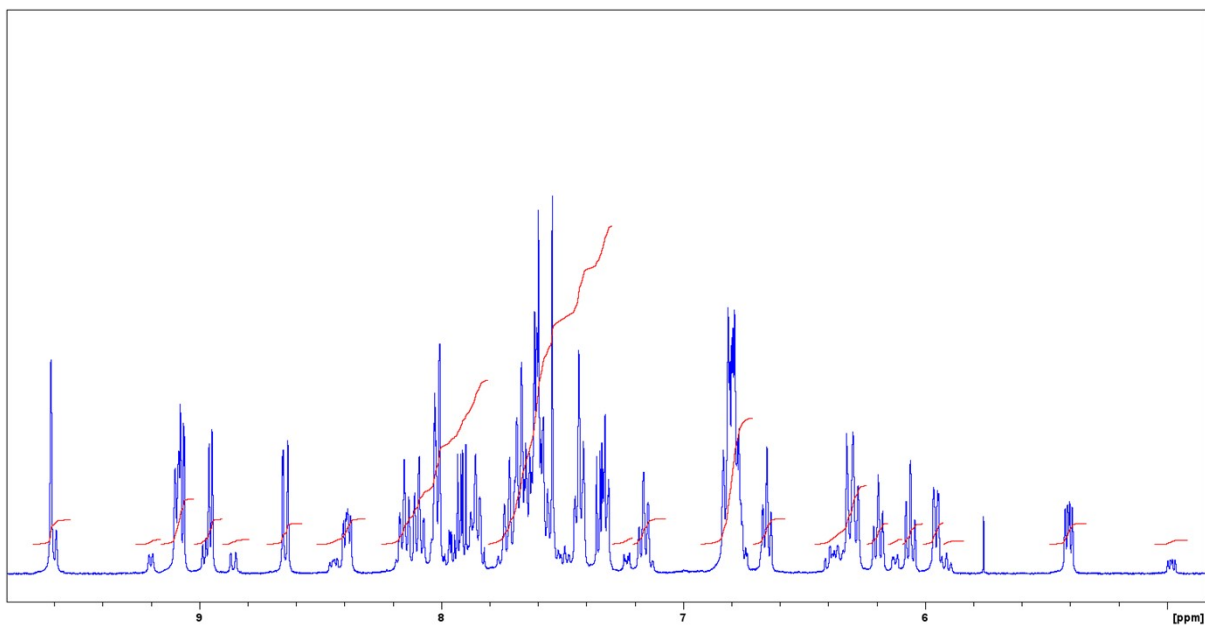


Figure S109. ^1H NMR spectra of IrPdL1 recorded at 400 MHz in d_6 -dmso.

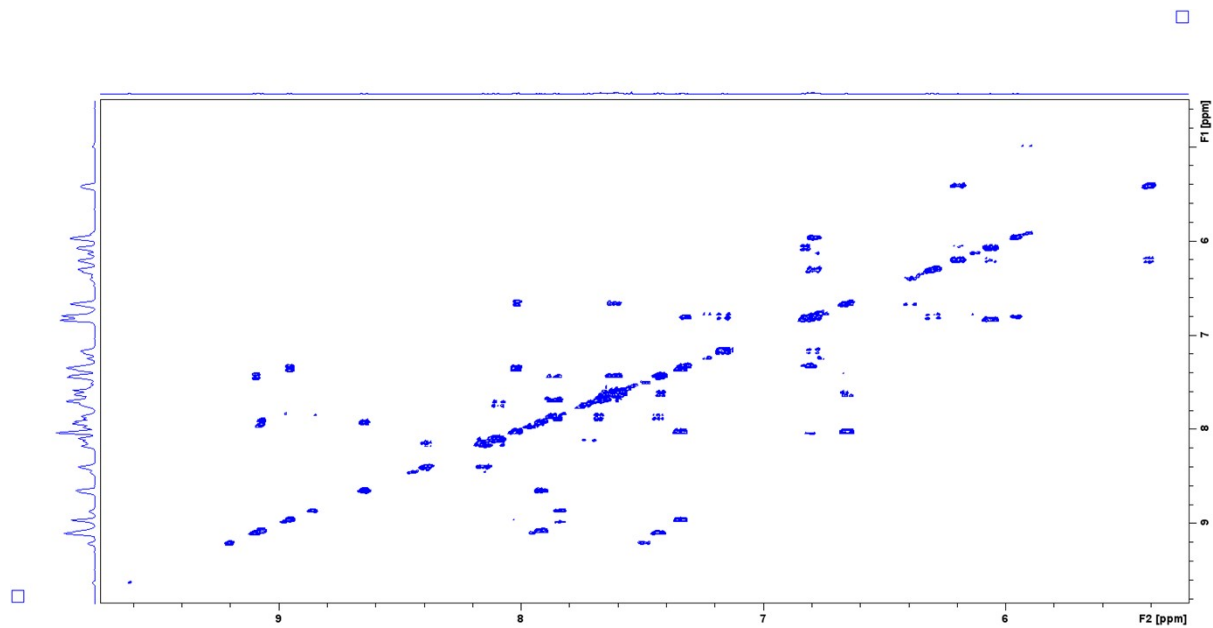


Figure S110. ^1H - ^1H COSY NMR spectrum of **IrPdL1** recorded at 400 MHz in d_6 -dmsol.

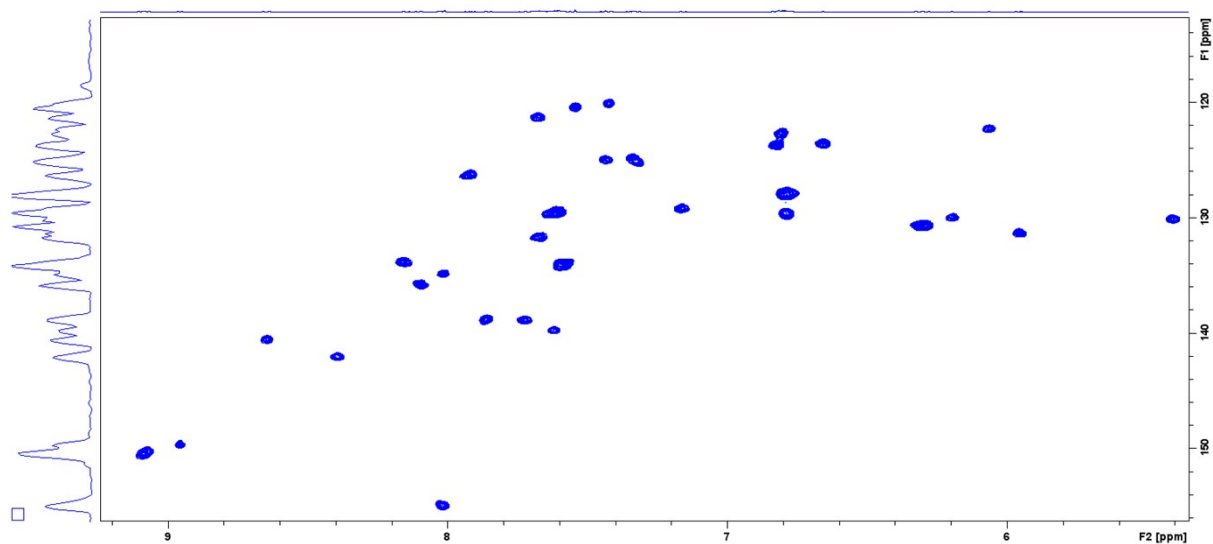


Figure S111. ^1H - ^{13}C HSQC NMR spectrum of **IrPdL1** recorded in d_6 -dmsol.

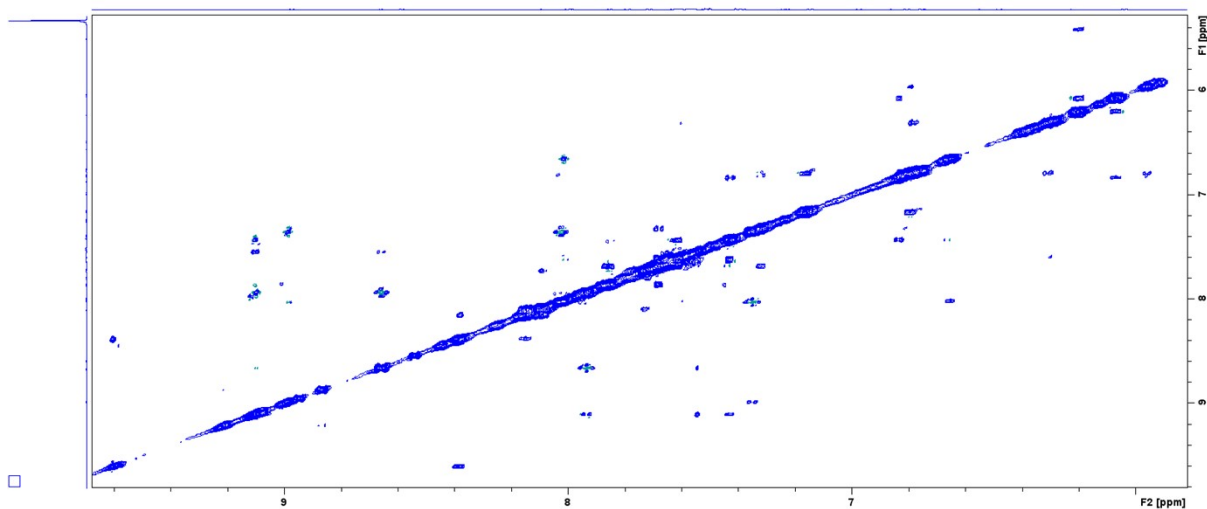
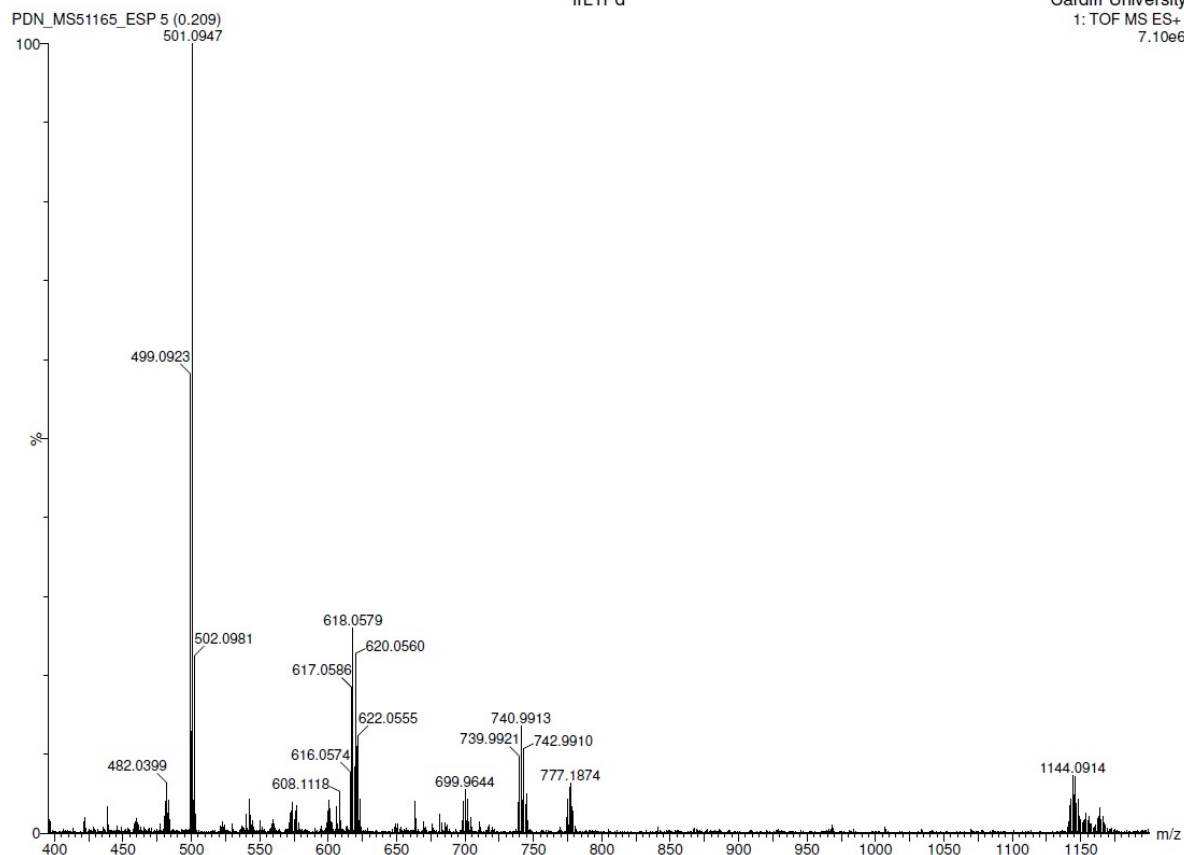


Figure S112. ^1H - ^1H NOESY NMR spectrum of IrPdL1 recorded at 400 MHz in d_6 -dmso.

21-May-2024 IrL1Pd XEVO-G2XSQT0F#NotSet
Cardiff University
1: TOF MS ES+
7.10e6



Minimum: -1.5
Maximum: 5.0 10.0 50.0

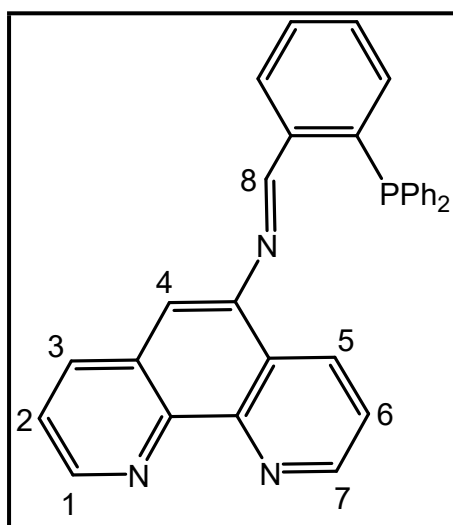
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1144.0914	1144.0906	0.8	0.7	38.0	1265.5	n/a	n/a	C53 H38 N5 P Cl2 Pd Ir

Figure S113. HRMS (ES^+) spectrum of IrPdL1.

	H1	H2	H3	H4	H5	H6	H7	H8
L1	9.01	7.49	7.99	6.64	8.25	7.44	9.09	9.09
ReL1	9.20	7.71	8.29	6.90	8.29	7.60	9.27	9.01
2ReL1	9.52	8.23	9.17	8.07		7.54	9.44	9.25
ReAuL1	9.17	7.76	8.60	7.51		7.50	9.20	9.02
RuL1	8.24	7.60	7.98	8.04	7.92		8.51	9.14
RuAuL1	8.20	7.75	8.53	7.55				9.14
IrAuL1	8.20	7.87	8.62	7.59	7.87	7.67	8.23	9.21
L2	8.80	7.39	7.88	6.61			9.00	
ReL2	8.85	7.69	8.23	6.50	8.79	7.84	9.25	
2ReL2	9.27	7.78	8.38	7.62	9.20	7.91	9.41	
ReAuL2	8.75		8.38	6.49	7.94		8.89	
RuAuL2								
IrAuL2	7.86	7.60	8.28	6.80	8.22	7.75	8.68	
AuL1	9.03		8.28	7.23	7.33	7.71	9.05	9.08
AuL2	8.72		7.67	6.33	8.17		8.95	
RePtL1	9.43 ^a	7.87	8.59	7.62	9.00	8.15	9.43 ^a	9.49
RePdL1	9.17 ^a	7.48	8.25	7.53	7.55	7.33	9.17 ^a	10.03
IrPdL1	9.09	7.43	8.64	7.54	8.95	7.33	9.07	9.62

^a overlapping

Table S1. ¹H NMR assignments (based on the structure below) for the aromatic hydrogens of the phenanthroline fragment in the ligands and complexes.



Spectroscopic data.

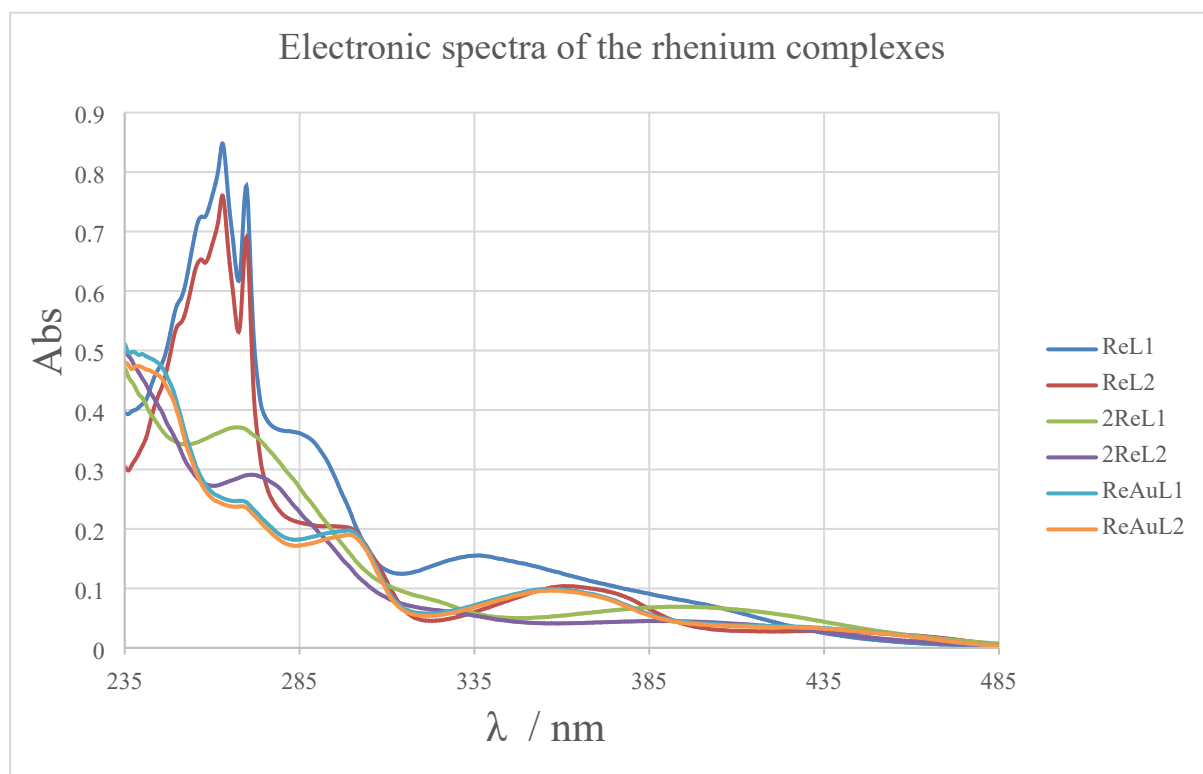


Figure S114. Electronic spectra of the rhenium complexes recorded as 1×10^{-5} M solutions in CH_2Cl_2 .

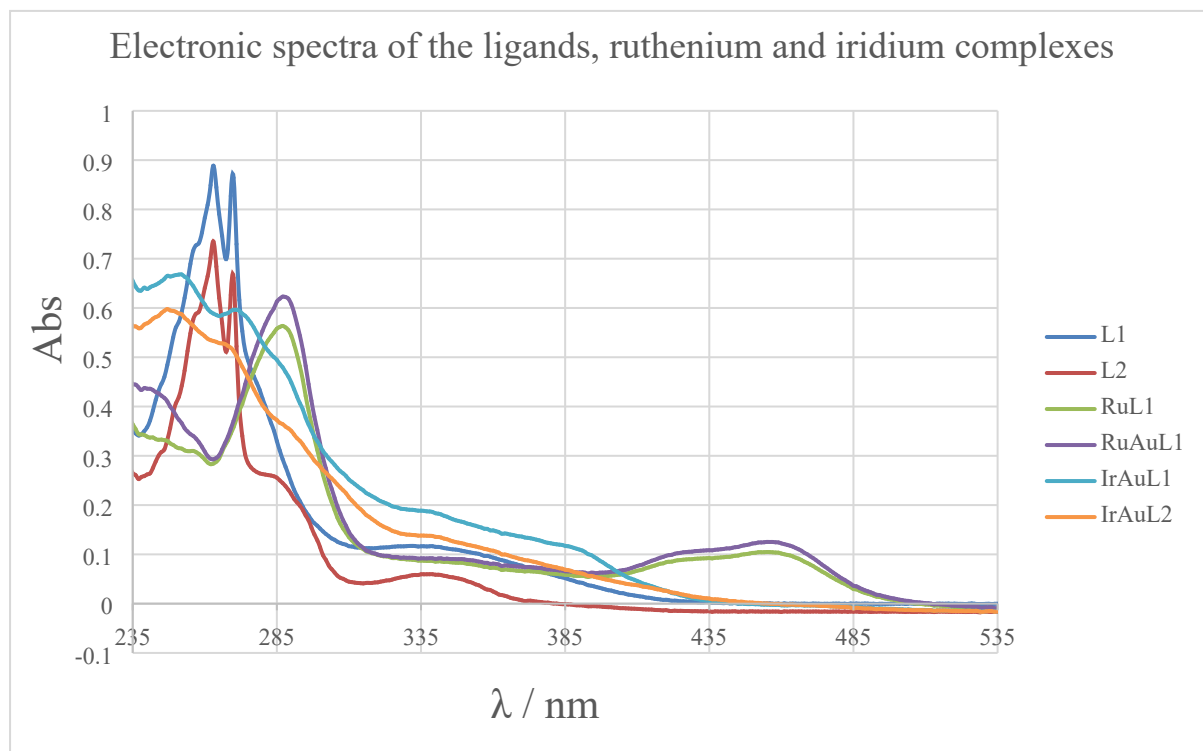


Figure S115. Electronic spectra of the ligands, ruthenium and iridium complexes recorded as 1×10^{-5} M solutions in CH_2Cl_2 .

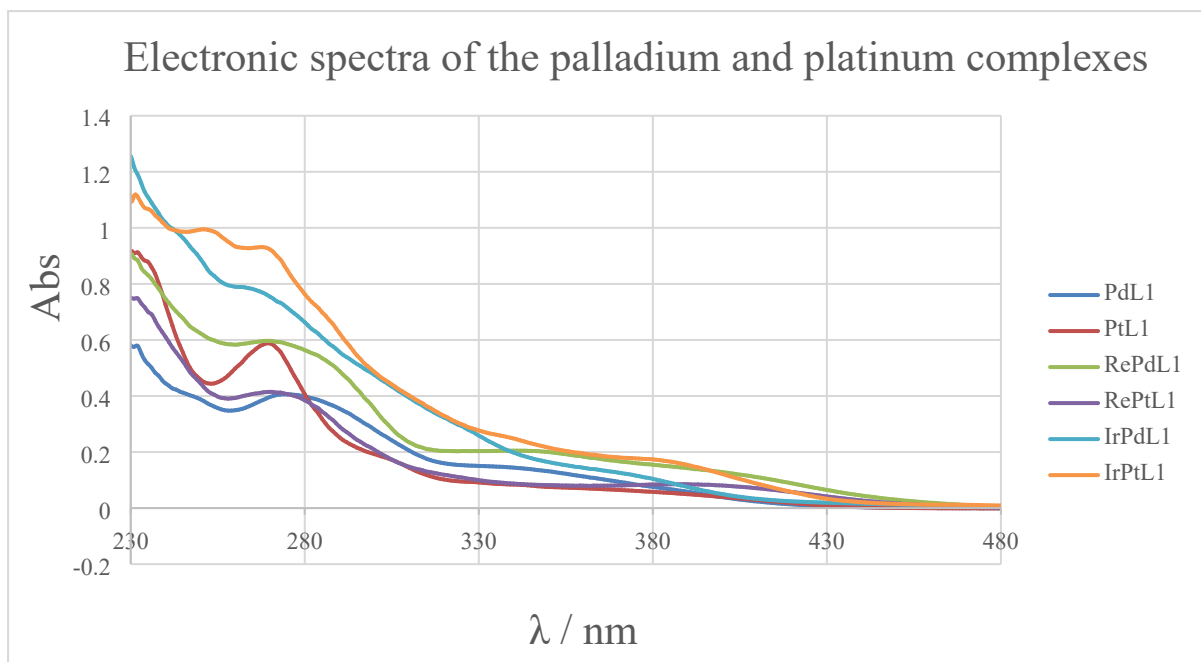


Figure S116. Electronic spectra of the palladium and platinum complexes recorded as 1×10^{-5} M solutions in CH_2Cl_2 .

Crystallographic data

Compound (Identification code)	2ReL1	2ReL2
CCDC reference		
Empirical formula	$C_{39}H_{26}Cl_6N_3O_6PRE_2$	$C_{43.5}H_{38}Cl_2N_3O_8PRE_2$
Formula weight	1248.70	1205.04
Temperature /K	293(2)	200(2)
Wavelength /Å	1.54184	1.54184
Crystal system	Monoclinic	Triclinic
Space group	P 2 ₁ /c	P -1
a/Å	15.8776(2)	11.0207(6)
b/Å	14.0772(6)	11.2629(5)
c/Å	19.3595(3)	20.4684(9)
α/°	90	87.135(4)
β/°	101.2970(10)	84.370(4)
γ/°	90	63.675(4)
Volume/Å ³	4243.25(11)	2266.1(2)
Z	4	2
Density (calculated)/ Mgm ⁻³	1.955	1.766
Absorption coefficient/ mm ⁻¹	15.232	12.148
SICrystal size/ mm ³	0.200x0.160x0.070	0.250x0.140x0.100
Reflections collected	8357	8777
Independent reflections	7286	6841
R(int)	0.0336	0.0393
Data / restraints / parameters	8357 / 0 / 514	8777 / 1070 / 686
Goodness-of-fit on F ²	1.020	1.076
R1, wR2 [I>2σ(I)]	0.0304, 0.0750	0.0391, 0.0971
R1, wR2 (all data)	0.0369, 0.0794	0.0570, 0.1117
Largest diff. peak and hole e.Å ⁻³	2.066 and -1.381	1.569 and -1.330

Table S2. Crystal data and structure refinement for **2ReL1** and **2ReL2**.

Compound (Identification code)	ReAuL2	AuL1
CCDC reference		
Empirical formula	C ₃₇ H ₂₇ AuCl ₁₁ N ₃ O ₃ PRE	C ₃₁ H ₂₂ AuClN ₃ P
Formula weight	1365.70	699.90
Temperature /K	200(2)	200(2)
Wavelength /Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
a/Å	10.9443(3)	9.7321(2)
b/Å	13.9344(4)	10.5512(3)
c/Å	16.9978(5)	14.1403(3)
α/°	74.830(2)	92.362(2)
β/°	78.584(2)	100.776(2)
γ/°	67.004(2)	112.287(3)
Volume/Å ³	2289.66(12)	1309.76(6)
Z	2	2
Density (calculated)/ Mgm ⁻³	1.981	1.775
Absorption coefficient/ mm ⁻¹	6.557	5.805
S1Crystal size/ mm ³	0.370x0.310x0.170	0.200x0.150x0.060
Reflections collected	11346	6479
Independent reflections	9144	5652
R(int)	0.0447	0.0424
Data / restraints / parameters	11346 / 487 / 626	6479 / 0 / 334
Goodness-of-fit on F ²	1.060	1.081
R1, wR2 [I>2σ(I)]	0.0399, 0.0995	0.0329, 0.0635
R1, wR2 (all data)	0.0543, 0.1109	0.0437, 0.0681
Largest diff. peak and hole e.Å ⁻³	1.759 and -1.505	1.319 and -1.161

Table S3. Crystal data and structure refinement for **ReAuL2** and **AuL1**.

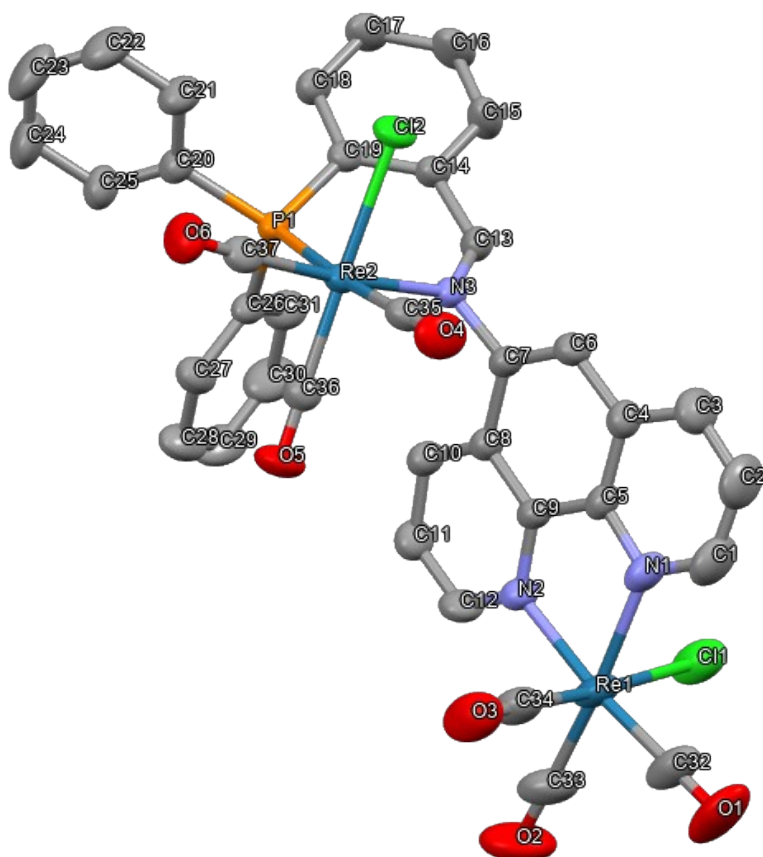


Figure S117. Molecular structure of **2ReL1**. Hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Re1-N1 2.176(4); Re1-N2 2.177(4); Re1-C32 1.916(6); Re1-C33 1.918(7); Re1-C23 1.939(6); Re1-Cl1 2.4734(14); Re2-N3 2.212(4); Re2-P1 2.4335(10); Re2-C35 1.968(5); Re2-C36 1.909(5); Re2-C37 1.933(5); Re2-Cl2 2.4868(10); N1-Re1-C33 171.9(2); N2-Re1-C32 174.1(2); Cl1-Re1-C34 176.02(18); N3-Re2-C37 173.61(16); P1-Re2-C35 174.73(14); Cl2-Re2-C36 177.27(14).

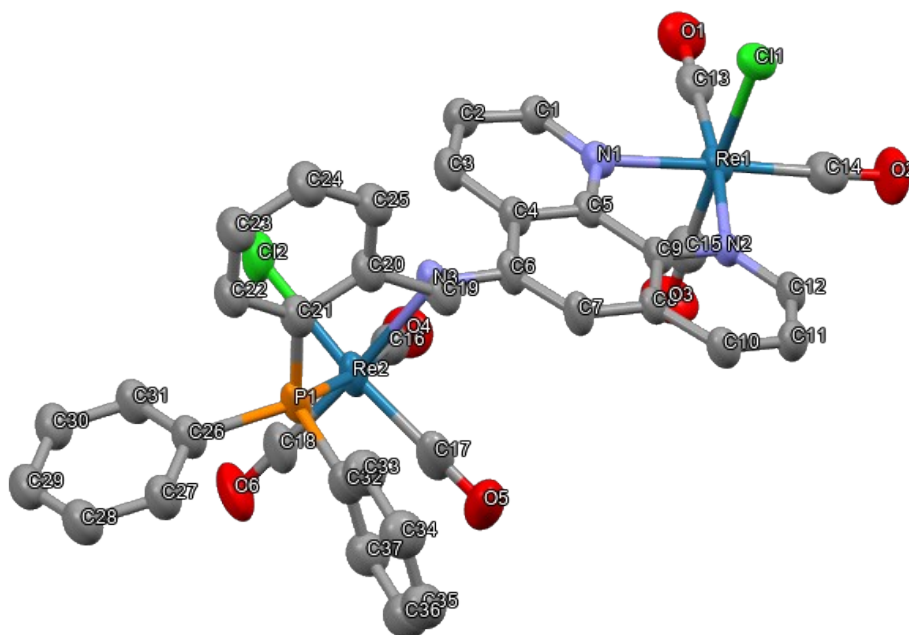


Figure S118. Molecular structure of **2ReL2**. Hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Re1–N1 2.190(5); Re1–N2 2.182(5); Re1–C13 1.925(7); Re1–C14 1.941(8); Re1–C15 1.917(9); Re1–Cl1 2.4779(16); Re2–N3 2.315(6); Re2–P1 2.491(2); Re2–C16 1.967(8); Re2–C17 1.902(9); Re2–C18 1.901(8); Re2–Cl2 2.4886(18); N2–Re1–C13 171.8(2); N1–Re1–C14 173.8(3); Cl1–Re1–C15 176.7(2); N3–Re2–C18 174.7(2); P1–Re2–C16 171.1(3); Cl2–Re2–C17 174.0(2).

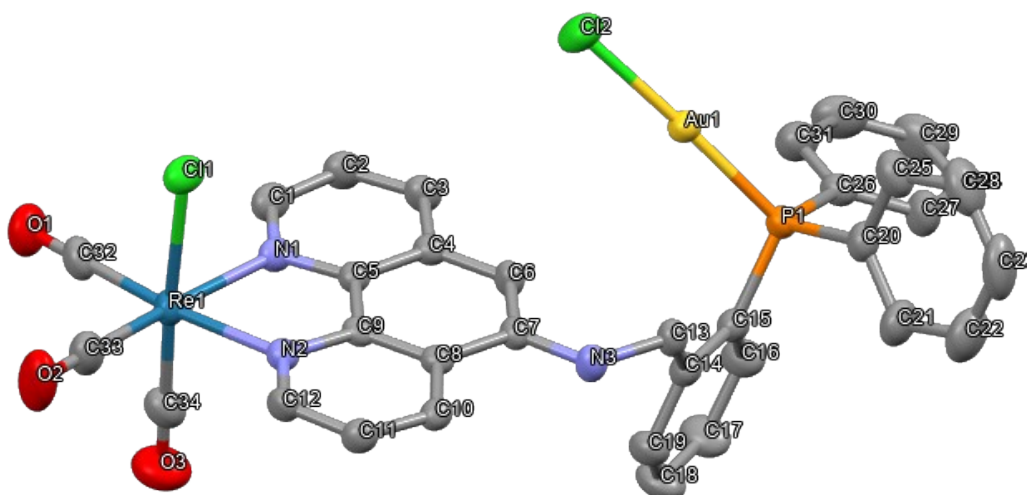


Figure S119. Molecular structure of **ReAuL2**. Hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Re1–N1 2.165(5); Re1–N2 2.191(5); Re1–C32 1.928(7); Re1–C33 1.913(7); Re1–C34 1.904(7); Re1–Cl1 2.4785(15); Au1–P1 2.2364(15); Au1–Cl2 2.2866(16); N1–Re1–C33 171.6(2); N2–Re1–C32 172.7(2); Cl1–Re1–C34 176.5(2); P1–Au1–Cl1 177.42(6).

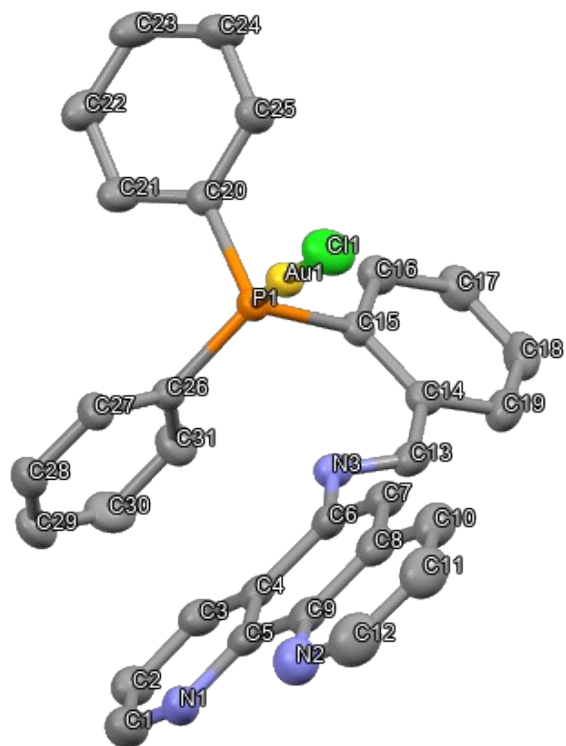


Figure S120. Molecular structure of **AuL1**. Hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au1-P1 2.2300(10); Au1-Cl1 2.2810(11); P1-Au1-Cl1 175.80(4).

Calculations

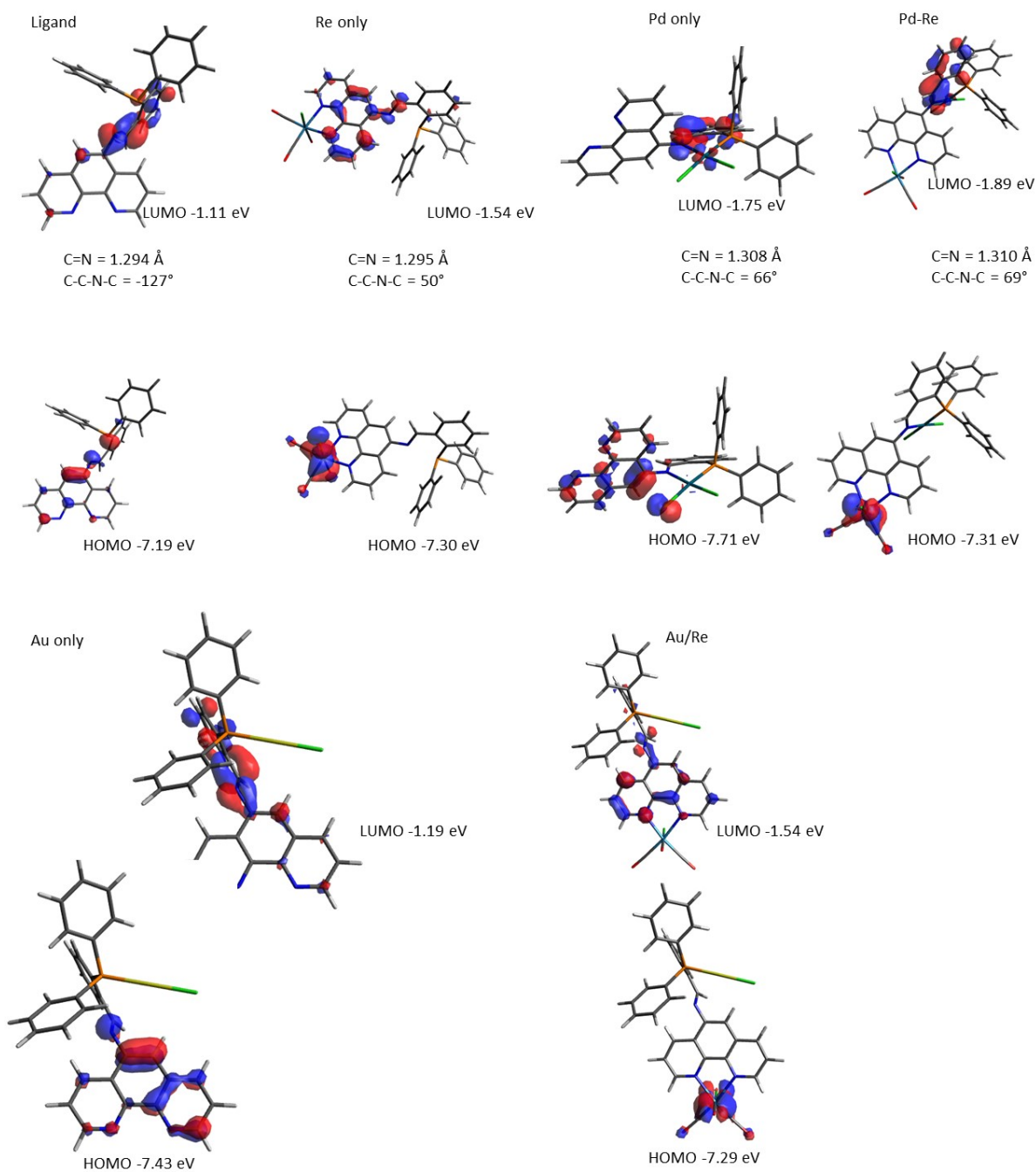
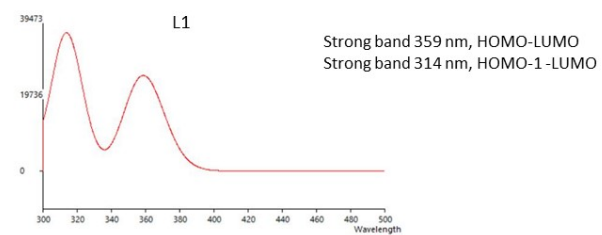
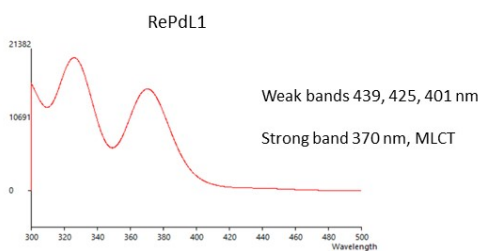
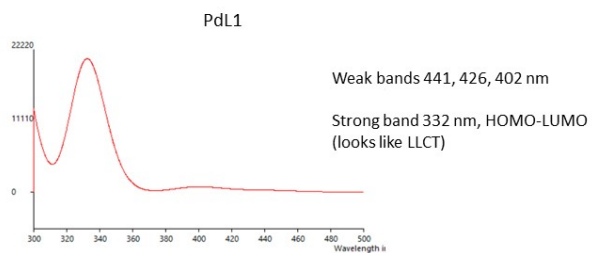
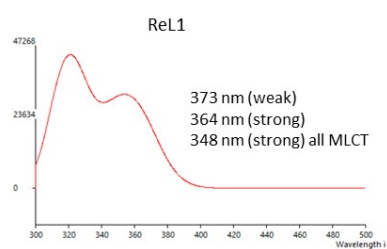


Figure S121. Calculated MOs for L1 and selected complexes.

Absorption in CH₂Cl₂
(CAM-B3LYP/def2svp)



Absorption in CH₂Cl₂
(CAM-B3LYP/def2svp)

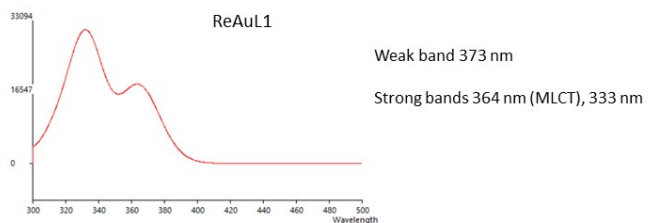
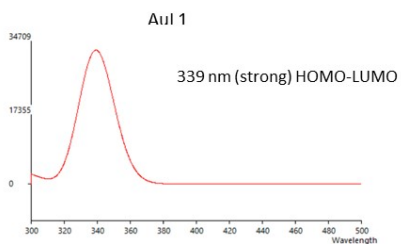


Figure S122. Calculated absorption spectra for **L1** and selected complexes.